Synthesis of enantiomerically pure thiocrown ethers derived from 1,1'-binaphthalene-2,2'-diol

Stock, H. Thijs; Kellogg, Richard M.

Published in:
Journal of Organic Chemistry

DOI:
10.1021/jo952107o

Publication date:
1996

Synthesis of Enantiomerically Pure Thiocrown Ethers Derived from 1,1′-Binaphthalene-2,2′-diol

H. Thijs Stock and Richard M. Kellogg*

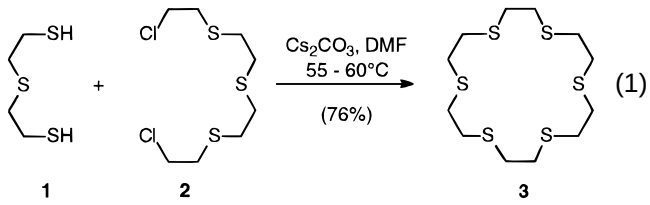
Department of Organic and Molecular Inorganic Chemistry, University of Groningen, Groningen 9747 AG, The Netherlands

Received November 28, 1995[⊗]

Synthetic methodology is given for the preparation of two different types of thiocrown ethers from optically pure 1,1′-binaphthalene-2,2′-diol (**10**). The conceptually simplest approach starts from optically pure **10** itself, which is alkylated (4 equiv of K_2CO_3 in DMF at 110 °C) with 2-chloroethanol followed by mesylation to provide 2,2′-bis(2-(mesyloxy)ethoxy)-1,1′-binaphthyl (**14**). When allowed to react with ethane-1,2-dithiol, propane-1,3-dithiol, 1,4,7-trithiaheptane, 1,4,8,11-tetrathiaundecane, 2,2-dimethylpropane-1,3-dithiol, 2-(mercaptomethyl)-1-propene-3-thiol, and 1,2-benzenedithiol in the presence of Cs_2CO_3 in DMF at 60 °C the corresponding thiocrown ethers **22**−**25**, **28**, **30**, and **32** are formed in 30−54% yields. Test reactions were carried out to establish that no racemization occurs during alkylation under these conditions. Reaction of optically pure **10** with tetrahydropyranyl (THP)-protected 3-chloropropanol under similar conditions for the preparation of **14** proceeded more sluggishly but cleanly. Removal of the THP protecting groups afforded 2,2′-bis(3-bromopropoxy)-1,1′-binaphthyl (**20**), which on reaction with propane-1,3-dithiol, 1,5,9-trithianonane, 2,2-dimethylpropane-1,3-dithiol, 2-(mercaptomethyl)-1-propene-3-thiol, and 1,2-bis(mercaptomethyl)benzene provided the respective thiocrown ethers **26**, **27**, **29**, **31**, and **33** in 24−68% yields. Another class of thiocrown ethers was prepared from optically active **10**, which was converted via ortho-lithiation to 3,3′-bis(bromomethyl)-2,2′-dimethoxy-1,1′-binaphthyl (**39**) by means of methylation (K_2CO_3/CH_3I), ortho-lithiation followed by formylation (*n*-C_4H_9Li/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA)/ether followed by DMF and H_2O workup) followed by reduction ($NaBH_4$) followed by bromination (PBr_3 in C_5H_5N). Reaction (Cs_2CO_3 in DMF at 60 °C) with 1,4,7-trithiaheptane, 1,4,8-trithiaoctane, 1,4,7,10-tetrathiadecane, 1,4,8,11-tetrathiaundecane, and 1,5,10,14-tetrathiatetradecane afforded the corresponding thiocrown ethers **40**−**44** in 40−75% yields. Despite repeated attempts using a wide range of reagents, demethylation of the methoxy ether functionalities failed. Attempts to prepare the free phenol derivatives of the latter type of crown ethers by oxidative coupling of two naphthol units failed.

Introduction

Investigations of crown ethers have been biased toward oxygen (ether) and nitrogen (amine) linkages at the cost of other heteroatoms like sulfur (sulfide).[1,2] In large part this state of affairs comes about from the lack, at least until fairly recently, of generally applicable and high yield syntheses for thiocrown ethers. The templated cyclizations[3] of ω-substituted alcohols and amines that work so well for the preparation of oxo- and azacrown ethers generally fail when thiolate is the nucleophile and the intermediate chain contains sulfide linkages. Attempts to use transition metals as synthetic templates for obtainment of thiocrown ethers have in general not been too successful.[4−6] In our hands, however, the use of Cs_2CO_3 in dimethylformamide (DMF) to generate cesium thiolates, which carry out nucleophilic substitutions on an appropriate chloride, bromide, mesylate, or other leaving group, has provided a satisfactory solution to the synthesis of many thiocrown ethers.[7,8] The method is illustrated in eq 1 for the synthesis of thio-18-crown-6 (**3**).



1 2 3 (1)

Thiocrown ethers have been studied chiefly for their capacity to ligate transition metal ions.[9] They bind second- and third-row transition metal ions and generally stabilize the lower oxidation states of these ions. Although sulfide linkages should have a significant affinity

* To whom correspondence should be addressed: Phone: +31-50-363 42 35. Fax: +31-50-363 42 96. E-mail: <R.M.Kellogg@rugch4.chem.rug.nl>.

⊗ Abstract published in *Advance ACS Abstracts,* April 1, 1996.

(1) *Crown Compounds. Towards Future Applications*; Cooper, S. R., Ed.; VCH Publishers: New York, 1992.

(2) For a review on the synthesis of crown ether compounds see: Okahara, M.; Nakatsuji, Y. In *Crown Ethers and Analogous Compounds*; Hiraoka, M., Ed.; Elsevier: Amsterdam, 1992; Chapter 2.

(3) (a) Mandolini, L.; Masci, B. *J. Am. Chem. Soc.* **1977**, *99*, 7709. (b) Ercolani, G.; Mandolini, L.; Masci, B. *J. Am. Chem. Soc.* **1981**, *103*, 2780. (c) Bowsher, B. R.; Rest, A. J. *Inorg. Chim. Acta* **1980**, *45*, L5. (d) Cacciapaglia, R.; Mandolini, L. *Chem. Soc. Rev.* **1993**, 221.

(4) For a review on early thiocrown ether syntheses see: Bradshaw, J. S.; Hui, J. Y. K. *J. Heterocycl.Chem.* **1974**, *11*, 649.

(5) (a) Dietrich, B.; Lehn, J.-M.; Sauvage, J. P. *J. Chem. Soc., Chem. Commun.* **1970**, 1055. (b) Alberts, A. H.; Annunziata, R.; Lehn, J.-M. *J. Am. Chem. Soc.* **1977**, *99*, 8502. (c) Vögtle, F.; Neumann, P.; Zuber, M. *Chem. Ber.* **1972**, *105*, 2955.

(6) Recently, we demonstrated that boric acid and a borium/aluminum isoproxide cocktail are effective templates in several thiocrown ether syntheses: (a) Edema, J. J. H.; Stock, H. T.; Buter, J.; Kellogg, R. M.; Smeets, W. J. J.; Spek, A. L. *Tetrahedron* **1993**, *49*, 4355. (b) Edema, J. J. H.; Stock, H. T.; Buter, J.; Kellogg, R. M.; Smeets, W. J. J.; Spek, A. L.; Van Bolhuis, F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 436.

(7) Buter, J.; Kellogg, R. M. *J. Chem. Soc., Chem. Commun.* **1980**, 466.

(8) (a) Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1981**, *46*, 4481. (b) Buter, J.; Kellogg, R. M. *Org. Synth.* **1987**, *65*, 1550.

(9) For reviews see: (a) Cooper, S. R. *Acc. Chem. Res.* **1988**, *21*, 141. (b) Cooper, S. R.; Rawle, S. C. *Struct. Bond. (Berlin)* **1990**, *72*, 1. (c) Blake, A. J.; Schröder, M. *Adv. Inorg. Chem.* **1990**, *35*, 1.

S0022-3263(95)02107-4 CCC: $12.00

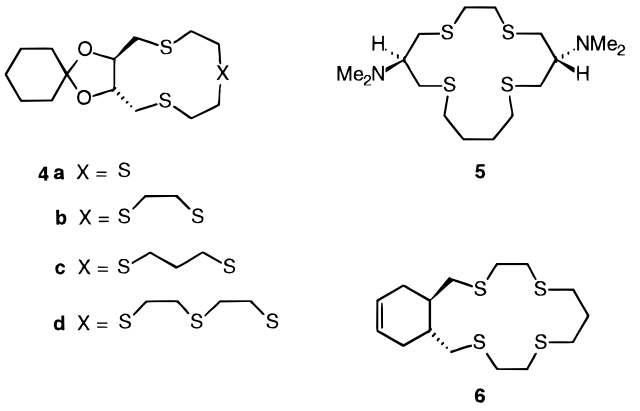


Figure 1.

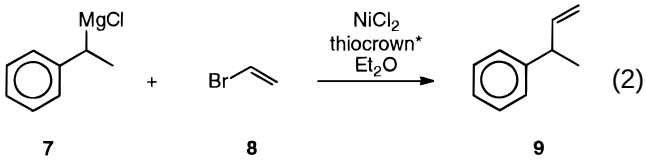
for such transition metal ions, the observed stability constants are often disappointingly small.[9] In general, thiocrown ethers show smaller macrocyclic effects than their corresponding oxo- and aza-analogs.[10,11] This is chiefly due to the tendency of the sulfide linkages to arrange themselves outside (exodentate) of the cavity.[12] The unit $-SCH_2CH_2S-$ tends toward an anticonformation rather than the gauche conformation favored by $-N(R)CH_2CH_2N(R)-$ and $-OCH_2CH_2O-$ segments.

Despite these conformational problems and their effect on complexation behavior, thiocrown ethers remain an interesting class of ligands. Both the capacity of sulfides to stabilize lower oxidation states of transition metal ions as well as the relative stability of sulfides compared to the more often used phosphines toward oxidation are obvious plus points. Moreover, sulfide linkages do not readily participate in protic equilibria as do amines. The possibility of "tuning" the coordination chemistry of thiocrown ethers by varying the ring size and the number of complexation sites is well within synthetic reach.[13] Application of *chiral nonracemic* thiocrown ethers as ligands for *asymmetric* syntheses catalyzed by a transition metal is also a potent area for application of these compounds, and the present work is intended as a step toward that goal.

At the time this work was initiated (1990) the only chiral nonracemic thiocrown ethers known were **4**−**6** (Figure 1).

Compounds **4** and **5** had been applied as ligands in the Ni(II)-catalyzed cross-coupling reaction of Grignard reagent **7** with vinyl bromide **8** (eq 2).[14] Although the chemical yields of **9** in this reaction were good to excellent, the asymmetric induction was only moderate. In the presence of 0.3 mol % thiocrown ether **5** the enantiomeric excess (ee) of **9** was 46%.

Chiral nonracemic thiocrown ethers have also been applied in the Zn(II)-catalyzed conjugate addition of



isopropylmagnesium bromide to cyclohexenone (not illustrated).[15] In this reaction **4b** and **6** were applied as ligands resulting in asymmetric inductions of 16 and 17% ee, respectively. These results are promising in terms of chemical reactivity but the challenge of obtaining high ee's is at the same time clear.

We describe here the syntheses of two new families of chiral nonracemic thiocrown ethers derived from 1,1′-binaphthalene-2,2′-diol.

Results

Axially dissymmetric 1,1′-binaphthalene-2,2′-diol (**10**) has been used as the chiral component for the preparation of all the compounds described here. There are two obvious retrosynthetic approaches to simple thiocrown ethers derived from **10** (Scheme 1, eq 3).

Path A is less attractive because of the need for β-chloro sulfides as the chain components; such compounds are powerful vesicants and *in our experience dangerous*. In our experience the use of leaving groups other than chloride does not provide a viable remedy to this problem. Attachment of two functionalized arms as shown in path B allows one to avoid this complication. Path B requires that bis-alkylation of **10** be achieved. We wanted to use commercially available enantiomerically pure **10**, rather than to synthesize racemic thiocrown ethers followed by optical resolution. For this reason racemization during the synthetic steps must be avoided. We noted, however, the report by Cram that enantiomerically pure **10** is 69% racemized when it is stirred for 23 h in a 0.67 M KOH solution in *n*-butanol at 118 °C and 72% racemized in a 1:1 mixture of dioxane and 20% aqueous HCl at 100 °C, but is optically stable under neutral conditions in dioxane−water at 100 °C.[16] Under sufficiently acidic or basic conditions the phenolic groups in **10** are charged, resulting in elongation of the biaryl bond, thereby diminishing the rotational barrier along this axis, making the molecule more prone to racemization. The possibility of racemization of **10** during alkylation (under basic conditions) obviously has to be checked.

Enantiomerically pure **10** (ee >99.9%, determined by HPLC) was alkylated by stirring a mixture of 1 equiv of **10** (0.067 M) and 4 equiv of ethyl bromide in the presence of 3 equiv of base at various temperatures in THF, DMF, acetone, acetonitrile, and DMF as solvents. Potassium *tert*-butoxide, NaH, and K_2CO_3 were used as bases. Both the ratio of monoalkylated product **11** to dialkylated **12** and the ee of **12** were examined (eq 4).

Under several conditions conversion to **12** was incomplete. However, to our relief, under none of the applied conditions was there more than 2% racemization. Even application of basic conditions at elevated temperatures did not result in substantial racemization. Under all investigated reaction conditions the first alkylation step, to give **11**, proceeds rapidly, whereas the second alkyla-

(10) (a) Smith, G. F.; Margerum, D. W. *J. Chem. Soc., Chem. Commun* **1975**, 807. (b) Sokol, L. S. W. S.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1981**, *20*, 3189. (c) Bach, R. D.; Vardhan, H. B. *J. Org. Chem.* **1986**, *51*, 1609.

(11) Microwave heating is sometimes required for effectuation of complex formation of thiocrown ethers: Baghurst, D. R.; Cooper, S. R.; Greene, D. L.; Mingos, D. M. P.; Reynolds, S. M. *Polyhedron* **1990**, *9*, 893.

(12) DeSimone, R. E.; Glick, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 762.

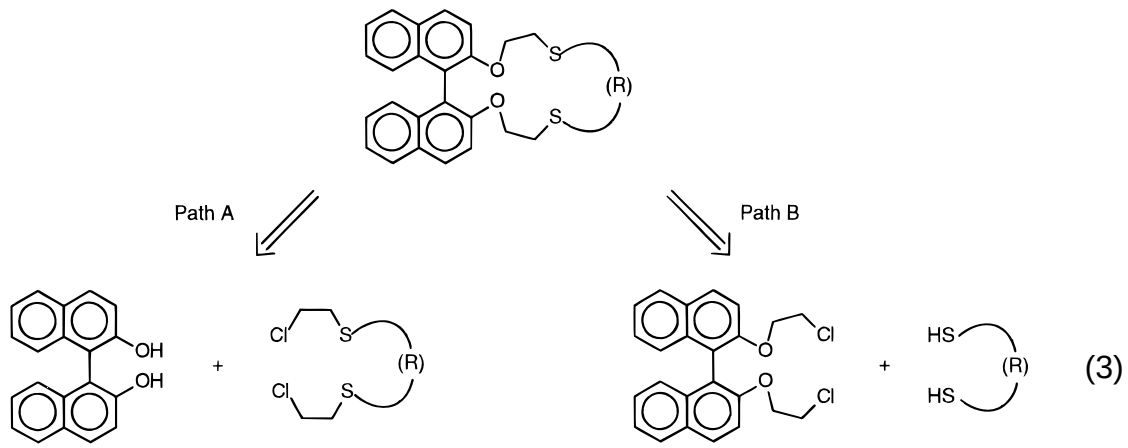
(13) Konno, T.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1988**, *27*, 4113.

(14) (a) Lemaire, M.; Buter, J.; Vriesema, B. K.; Kellogg, R. M. *J. Chem. Soc., Chem. Commun.* **1984**, 309. (b) Vriesema, B. K.; Lemaire, M.; Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1986**, *51*, 5169. (c) Vriesema, B. K. Ph.D. Thesis, University of Groningen, the Netherlands, 1986, Chapter 4.

(15) Jansen, J. F. G. A.; Feringa, B. L. *J. Org. Chem.* **1990**, *55*, 4168.

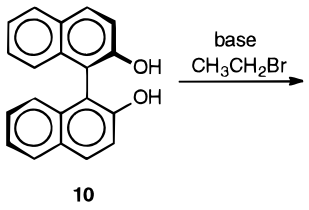
(16) (a) Kyba, E. B.; Koga, K.; Sousa, L. R.; Siegel, M. G.; Cram, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 2692. (b) Kyba, E. P.; Gokel, G. W.; De Jong, F.; Koga, K.; Sousa, L. R.; Siegel, M. G.; Kaplan, L.; Sogah, G. D. Y.; Cram, D. J. *J. Org. Chem.* **1977**, *42*, 4173.

Scheme 1

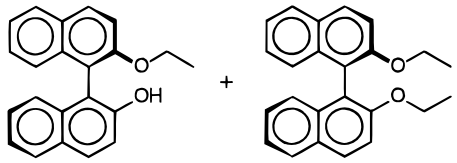


(3)

tion step, giving **12**, is much slower. Thus, during the reaction there is a high concentration of **11**. Apparently,

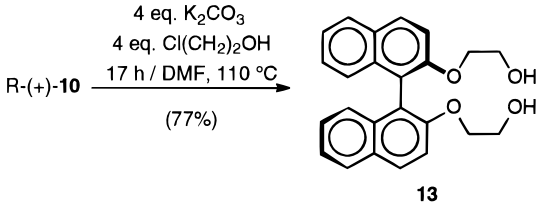


10

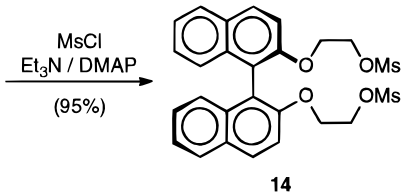


11 **12** (4)

the rate of racemization of mono-alkylated **11** under basic conditions at elevated temperatures is very low and the rate of mono-alkylation of **10** is much higher than its rate of racemization. After considerable experimentation[17] it was found that the optimized reaction conditions for bis-ethylation of **10** are the use of K_2CO_3 as base in DMF at a temperature of 110 °C. Under these conditions **12** was obtained in 100% yield and 99.6% ee.



13 (5)



14

On applying these reaction conditions to the reaction of **10** with 2-chloroethanol as alkylating agent **13** was obtained in 77% yield (eq 5).

A somewhat higher yield (89%) of bis-alkylated product was obtained by using THP-protected 2-chloroethanol as alkylating agent, but after deprotection with HCl the total yield of **13** was not higher than the single step shown in eq 5. Bis-mesylation of **13** was achieved by reaction with mesyl chloride and triethylamine in the presence of 4-(*N*,*N*-dimethylamino)pyridine (DMAP) as nucleophilic catalyst.

The ligating properties of thiocrown ether ligands can be tuned by varying both the ring-size and the positioning of the heteroatoms within the crown ether. To prepare more flexible thiocrown ethers dibromide **20**, a homologue of **14** with a chain length of three carbon atoms instead of two was required. The synthesis of **20** turned out to be troublesome. The routes examined are summarized in eq 6 (Scheme 2).

Alkylation of **10** was carried out with 3-chloro-1-propanol in DMF at 110 °C. Although 4 equiv of chloride and of base was used, considerable amounts of mono-alkylated product **16** were obtained. The yield of bis-alkylated **15** after purification could not be raised above 59%. The problem was traced to the competitive formation of 7-chloro-4-oxaheptanol (**17**). This complication was avoided by use of THP-protected **18**; bis-alkylated product **19** was obtained as a mixture of diastereomers in 89% yield and the deprotection step delivered **15** in 95% yield. Bromination of **15** with PBr_3/pyridine was, however, unsatisfactory and provided **20** in only 19% yield. Reaction of THP ethers with $LiBr/BF_3{\cdot}Et_2O$ or $LiBr/ClSiMe_3$ are reported to provide directly the halides;[18] however, with **19** only undefinable products were found. An excellent solution to this problem was found in the method of Schwarz et al.[19] whereby THP ether **19** was brominated directly with triphenylphosphonium bromide; the dibromide **20** was isolated in 73% yield. A disadvantage of this reaction, especially when performed on larger scale, is the huge amount of triphenylphosphine oxide produced. This byproduct can be removed, however, by crystallization from toluene/*n*-octane. The triphenylphosphine oxide is washed thoroughly with *n*-hexane to recover any remaining **20**, which is then purified by column chromatography.

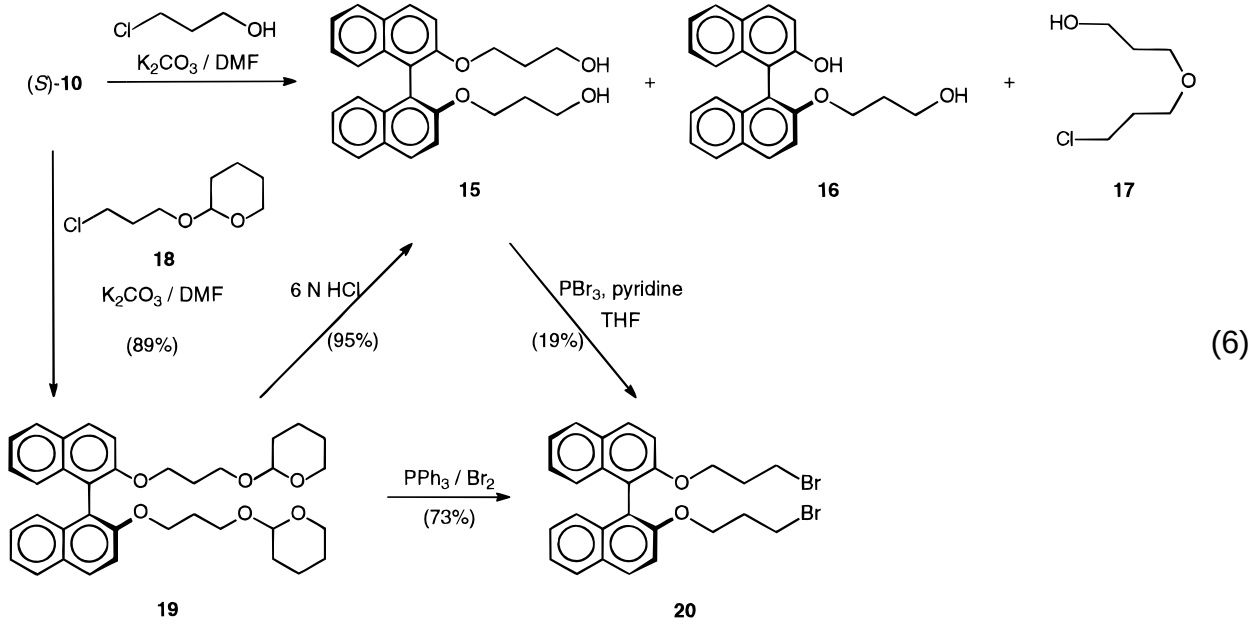
The procedure used for ring-closure is illustrated for the preparation of **22** in eq 7. Cyclization of **14** with 1,3-

(17) Full details of the investigated procedures can be found in: Stock, H. T. Ph.D. Thesis, University of Groningen, the Netherlands, 1994.

(18) (a) Vankar, Y. D.; Shah, K. *Tetrahedron Lett.* **1991**, *32*, 1081. (b) Sato, T.; Tada, T.; Otera, J.; Nozaki, H. *Tetrahedron Lett.* **1989**, *30*, 1665.

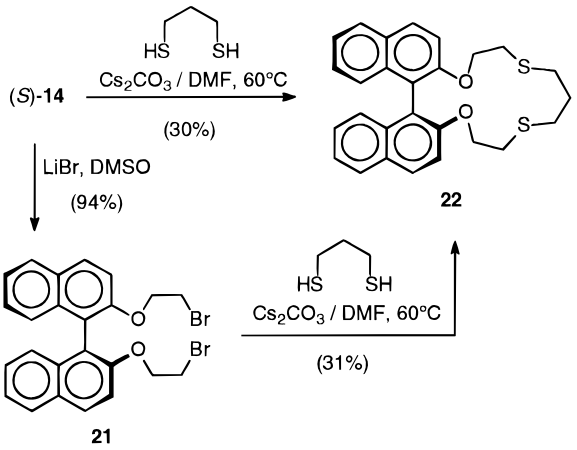
(19) Schwarz, M.; Oliver, J. E.; Sonnet, P. E. *J. Org.Chem.* **1975**, *40*, 2410.

Scheme 2



(6)

propanedithiol by use of the Cs_2CO_3/DMF method[7,8] afforded thiocrown ether **22** in 30% yield. Ring strain in **22** is probably the reason for the only moderate yield. Change of leaving group did not help; analogous cyclization of dibromide **21**, obtained from **14** by reaction with LiBr in DMSO at 60 °C, gave **22** in essentially the same yield (eq 7).



(7)

The thiocrown ethers **23**−**25** were synthesized in an analogous manner by cyclization of bis-mesylate **14**. Isolated yields are given in parentheses. The propylene bridged thiocrown ethers **26** and **27** were prepared from **20**. The appropriate dithiols were either commercially available or were prepared by routes well described in the literature (Figure 2).

Desper and Gellman have used *gem*-dimethyl units in the backbone of thiocrown ethers to achieve rigidity and preorganization for complexation of metal ions.[20] Analogously, we prepared **28** and **29**. Compound **29** complexed 1 equiv of ethanol on recrystallization from that solvent. The structure of the complex is not known. The ethanol could be removed by column chromatography over silica gel using toluene/n-hexane as eluent. Macrocycles **30**−**33**, with other incorporated units, were prepared starting from either **14** or **20**.

In order to check whether racemization had occurred during any of the synthetic steps used in preparation of the thiocrown ethers the ee of **24** was determined. HPLC analysis on a Daicel OT$^+$ column showed the ee be 99.5%, so no racemization had occurred. We assume this to be general for all thiocrown ether syntheses described here, especially since the conditions for alkylation have been shown not to lead to racemization.

With the intention of maintaining the phenolic groups of **10** for binding, the synthesis from **10** of 3,3′-substituted bis-naphthol systems **34** was examined. A simple retrosynthesis is given in eq 8.

Cram has described the synthesis of racemic 3,3′ disubstituted **35** (X = morpholine, R = H) by a Mannich reaction, but the prolonged high temperatures required (5 days at 160 °C) would lead to racemization of optically active **10**.[21,22] Cram has also reported the preparation of enantiomerically pure **35** (X = OH, R = H) via an oxidative coupling of 2-hydroxynaphthalene-3-carboxylic acid followed by resolution and reduction. The overall yield (21%) is low, however, and we sought an alternative approach to enantiomerically pure **35**.

In initial attempts to achieve 3,3′ functionalization of **10** Vilsmeier−Haack conditions ($POCl_3$/DMF), the Reimer−Tiemann reaction (75% NaOH/$CHCl_3$), reaction with paraformaldehyde, $SnCl_4$, and 2,6-lutidine,[23] and the Fries rearrangement of the bis-benzoate[24] of **10** were tried. All these approaches in our hands failed.[25] More

(20) (a) Desper, J. M.; Gellman, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 6732. (b) Desper, J. M.; Gellman, S. H. *J. Am. Chem. Soc.* **1991**, *113*, 704. (c) Desper, J. M.; Gellman, S. H.; Wolf, R. E.; Cooper, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 8663. (d) Nazarenko, A. Y.; Izatt, R. M.; Lamb, J. D.; Desper, J. M.; Matysik, B. E.; Gellman, S. H. *Inorg. Chem.* **1992**, *31*, 3990. (e) Desper, J. M.; Vyvyan, J. R.; Mayer, M. J.; Ochrymowycz, L. A.; Gellman, S. H. *Inorg. Chem.* **1993**, *32*, 381.

(21) (a) Koenig, K. E.; Helgeson, R. C.; Cram, D. J. *J. Am. Chem. Soc.* **1976**, *98*, 4018. (b) Helgeson, R. C.; Tarnowski, T. L.; Cram, D. J. *J. Org. Chem.* **1979**, *44*, 2538.

(22) Cram, D. J.; Helgeson, R. C.; Peacock, S. C.; Kaplan, L. J.; Domeier, L. A.; Moreau, P.; Koga, K.; Mayer, J. M.; Chao, Y.; Siegel, M. G.; Hoffman, D. H.; Sogah, G. D. Y. *J. Org. Chem.* **1978**, *43*, 1930.

(23) Casiraghi; Casnati; Puglia; Sartori; Terenghi *J. Chem. Soc., Perkin Trans. 1* **1980**, 1862.

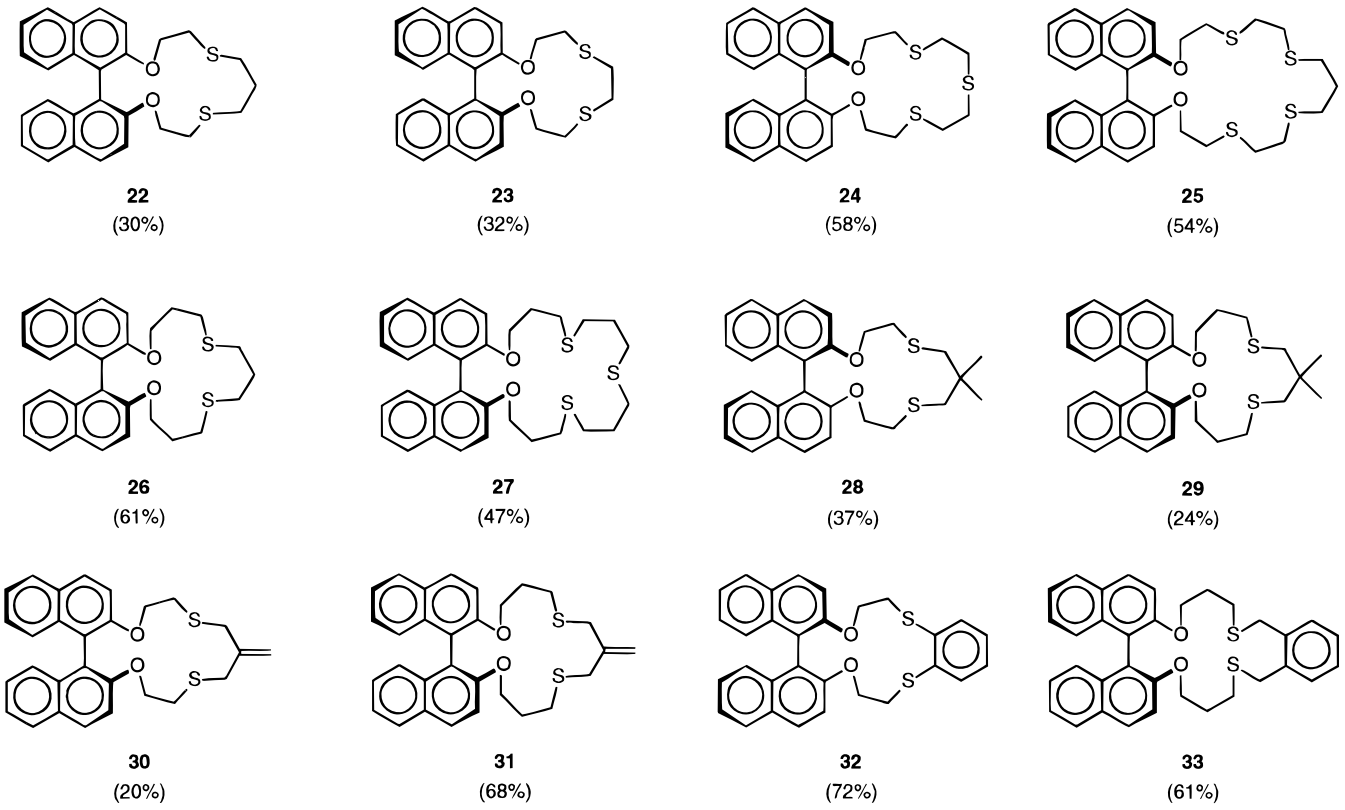
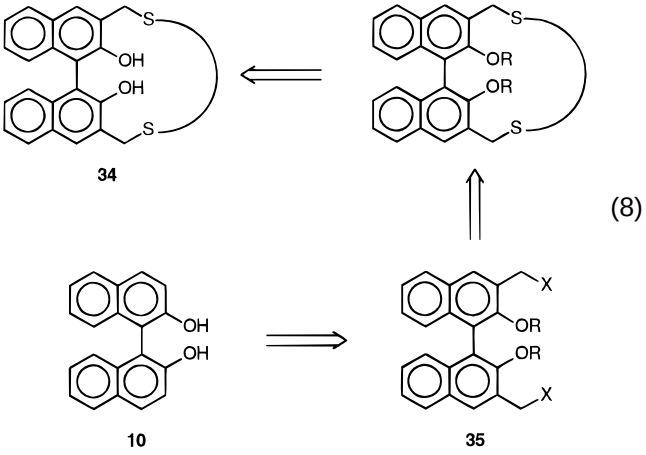
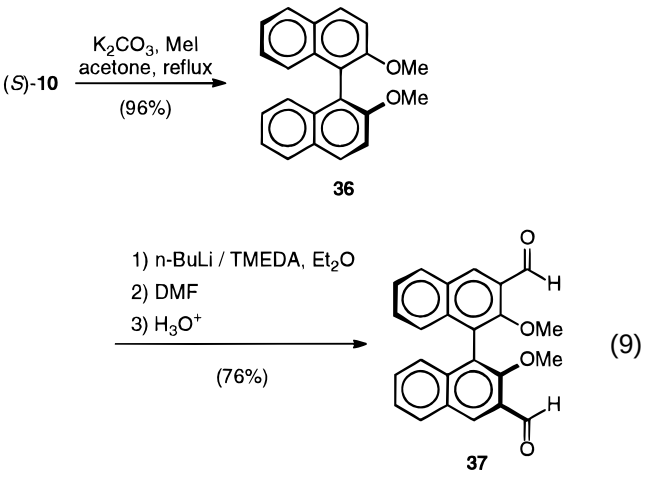


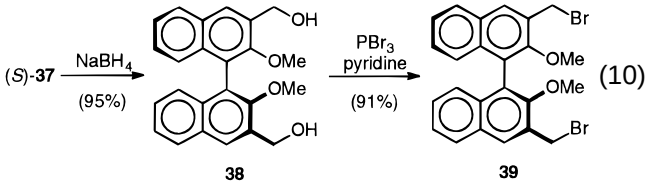
Figure 2.



success was obtained via an ortho-lithiation route as illustrated in eq 9.[26]



To achieve lithiation O-methylation (96%) of **10** was necessary. Ortho-lithiation of **36** with *n*-BuLi in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) in THF at 0 °C led to the desired product **37**, but the yield was only 24%. Contemporary with our work Naruta and co-workers[27] described the synthesis of the 3,3′-bis-carboxylate of **36** via ortho-lithiation of **36** in refluxing diethyl ether as solvent. When these conditions were applied and the bis-lithiated **36** was allowed to react with DMF, bis-aldehyde **37** was obtained in 76% yield. HPLC analysis established that **37** was enantiomerically pure. Reduction to **38** (95%) and bromination (91%) (eq 10) provided dibromide **39** in 63% overall yield starting from **10**.



The thiocrown ethers **40**−**44** were prepared in 40−76% yield using the cesium thiolate approach described previously (Figure 3).

Unfortunately, we were completely stymied in our attempts to demethylate these thiocrown ethers. A brief description is given of the attempts that have been made following many of the known protocols for demethylating

(24) Badr, M. Z. A.; Aly, M. M.; Abdel-Latif, F. F. *J. Org. Chem.* **1979**, *44*, 3244.
(25) See also: Moneta, W.; Baret, P.; Pierre, J.-L. *Bull. Soc. Chim. Fr.* **1988**, 995.
(26) (a) Narasimhan, N. S.; Mali, R. S. *Synthesis* **1983**, 957. (b) Gschwend, H. W.; Rodriquez, H. R. *Org. React.* **1979**, *26*, 35.
(27) Naruta, Y.; Tani, F.; Ishihara, N.; Maruyama, K. *J. Am. Chem. Soc.* **1991**, *113*, 6865.

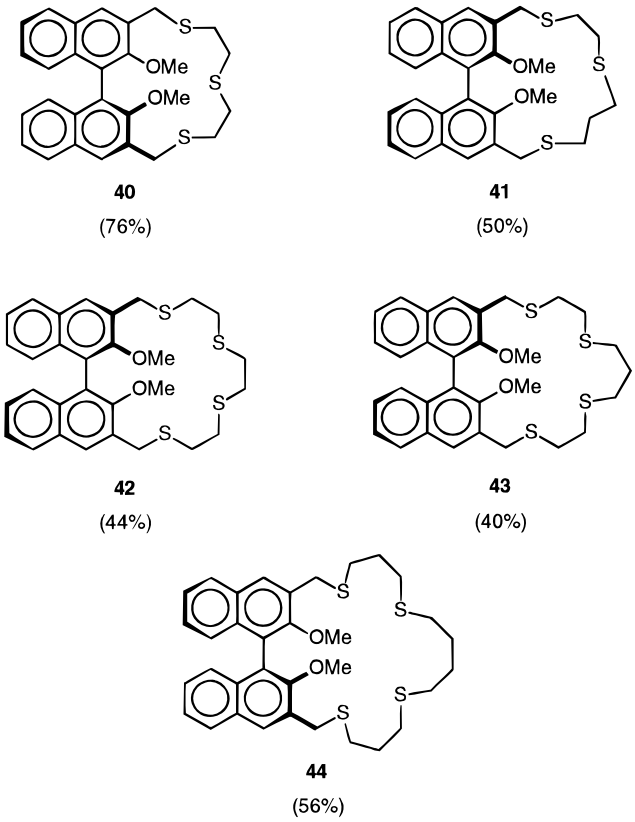


Figure 3.

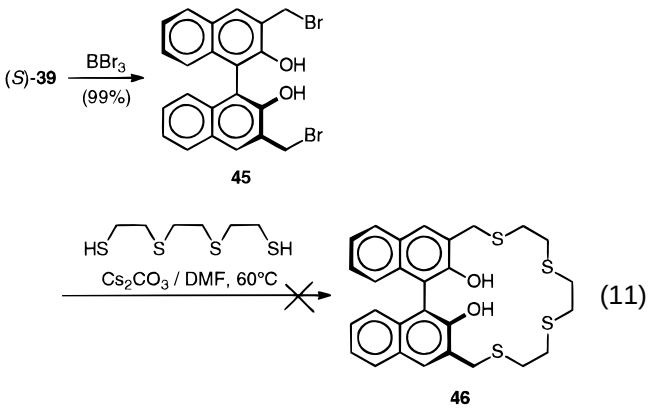
Table 1. Attempted Demethylation of Intraannular Methoxy Groups

entry	substrate	conditions	product(s)
1	**40**	48% HBr, AcOH, reflux, 1 h	complex mixture
2	**40**	48% HBr, AcOH, 50 °C, 6 h	starting material
3	**42**	48% HBr, AcOH, 100 °C, 1 h	complex mixture
4	**40**	2 equiv of BBr_3, CH_2Cl_2, 0 °C, 4 h	starting material
5	**40**	12 equiv of BBr_3, CH_2Cl_2, reflux, 18 h	starting material
6	**40**	12 equiv of BBr_3, CCl_4, reflux, 18 h	starting material
7	**42**	12 equiv of BBr_3, CH_2Cl_2, reflux, 18 h	starting material
8	**40**	KI, Me_3SiCl, CH_3CN, reflux, 44 h	starting material
9	**42**	KI, Me_3SiCl, CH_3CN, reflux, 20 h	starting material
10	**42**	pyridine·HCl, reflux, 3 h	complex mixture
11	**40**	EtSNa, DMF, reflux, 2 h	complex mixture
12	**43**	EtSNa, DMF, 100 °C, 2 h	starting material
13	**40**	NaCN, DMSO, 180 °C, 16 h	starting material
14	**42**	LiI, pyridine, reflux, 3 d	starting material
15	**42**	AgI, pyridine, reflux, 24 h	starting material
16	**40**	AgCN, DMSO, 100 °C, 48 h	starting material
17	**40**	AgCN, DMSO, reflux, 72 h	complex mixture, containing **37**
18	**40**	$LiAlH_4$, THF, reflux, 20 h	starting material
19	**42**	$LiAlH_4$, THF, reflux, 20 h	starting material

aryl methyl ethers.[28] Various conditions used for attempted demethylation are summarized in Table 1.

HBr and acetic acid (Table 1, entries 1−3) led either to no reaction or destruction of the ring systems.[29] BBr_3 (Table 1, entries 4−7) even in large excess failed to cause any reaction.[30] The same is true of $(CH_3)_3SiI$ (Table 1, entries 8 and 9).[31] Attempted reactions using other nucleophiles (Table 1, entries 10−13) either led to destruction of the ring system or no reaction.[32−34] McKervey *et al.* found that oxocrown ethers are readily demethylated by LiI in what appears to be an example of catalysis by a crown ether.[35] Reinhoudt *et al.* report, however, that larger ring crown ethers fail to demethylate under these conditions.[36,37] When these conditions were applied to thiocrown ether **42** no reaction took place (Table 1, entry 14). Attempts to use cations other than lithium (Table 1, entries 15−17) were to no avail. Bartsch *et al.* have reported the use of $LiAlH_4$ in refluxing THF for deprotection of aryl methyl ethers incorporated in oxocrown ethers.[38] Unfortunately, no reaction was obtained using these conditions (Table 1, entries 18 and 19).

In view of these failures we turned to routes whereby methyl ethers are not used for protection of the phenolic groups. To check whether it is necessary to protect the phenolic groups **45** was prepared by deprotection of **39** with BBr_3 (eq 11). Not unsurprisingly, attempts to



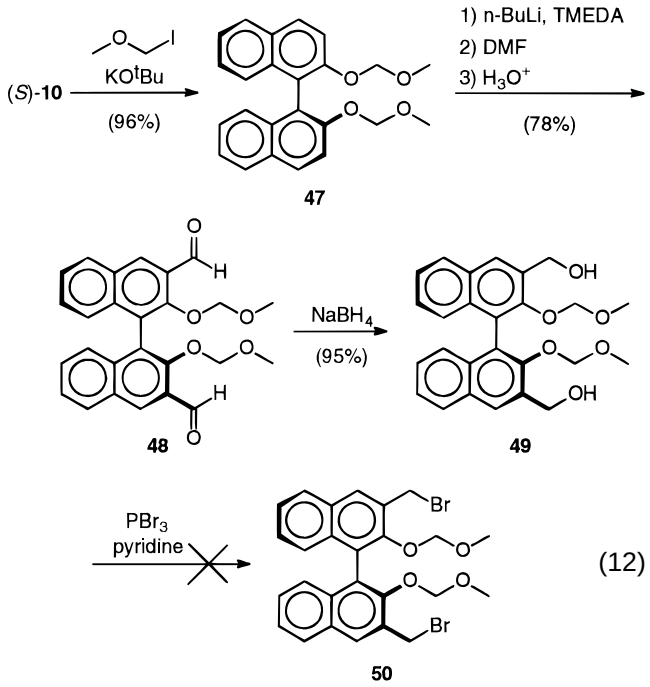
cyclize **45** to **46** failed. Reaction took place readily, but a complex mixture was obtained, from which no products could be characterized.

The MOM protective group was next investigated as summarized in eq 12.

Preparation of the bromide **50** (other leaving groups were also examined) fails undoubtedly because of its intrinsic instability due to intramolecular participation

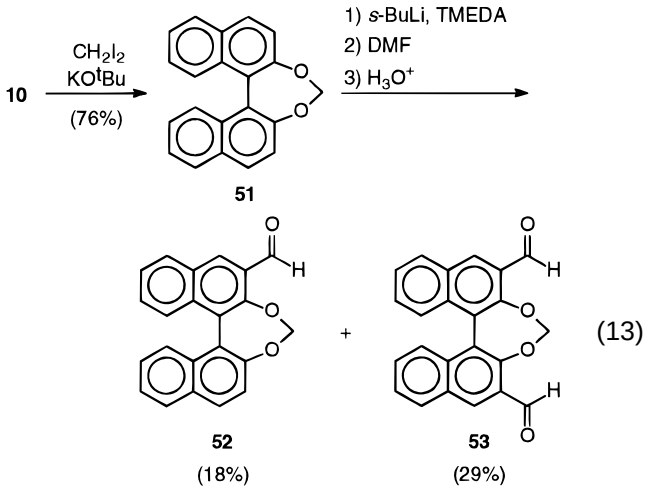
(28) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley & Sons: New York, 1991; Chapter 3, pp 145−149.

(29) Kawasaki, I.; Matsuda, K.; Kaneko, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1986.
(30) (a) McOmie, J. F. W.; West, D. E. *Organic Synthesis*; Wiley: New York, 1973; p 412. (b) Akimoto, H.; Yamada, S. *Tetrahedron* **1971**, *27*, 5999. (c) Tétreau, C.; Lavalette, D.; Cabaret, D.; Geraghty, N.; Welvart, Z. *J. Phys. Chem.* **1983**, *87*, 3234. (d) McOmie, J. W. F.; Watts, M. L.; West, D. E. *Tetrahedron* **1968**, *24*, 2289.
(31) (a) Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3761. (b) Olah, G. A.; Narang, S. C. *Tetrahedron* **1982**, *38*, 2225. (c) Olah, G. A.; Narang, S. C.; Balaram Gupta, B. G.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247.
(32) Curphey, T. J.; Hoffman, E. J.; McDonald, C. *Chem. Ind.* **1967**, 1138.
(33) a) Feutrill, G. I.; Mirrington, R. N. *Aust. J. Chem.* **1972**, *25*, 1719. (b) Feutrill, G. I.; Mirrington, R. N. *Tetrahedron Lett.* **1970**, 1327.
(34) McCarthy, J. R.; Moore, J. L.; Crege, R. J. *Tetrahedron Lett.* **1978**, 5183.
(35) Browne, C. M.; Ferguson, G; McKervey, M. A.; Mulholland, D. L.; O'Connor, T.; Parvez, M. *J. Am. Chem. Soc.* **1985**, *107*, 2703.
(36) Van der leij, M.; Oosterink, H. J.; Hall, R. H.; Reinhoudt, D. N. *Tetrahedron* **1981**, *37*, 3661.
(37) De Jong, F.; Reinhoudt, D. N. *Adv. Phys. Org. Chem.* **1980**, *17*, 279.
(38) (a) Czech, B. P.; Huh, H.; Bartsch, R. A. *J. Org. Chem.* **1992**, *57*, 725. (b) Czech, A.; Czech, B. P.; Desai, D. H.; Hallman, J. L.; Phillips, J. B.; Bartsch, R. A. *J. Heterocycl. Chem.* **1986**, *23*, 1355.



(12)

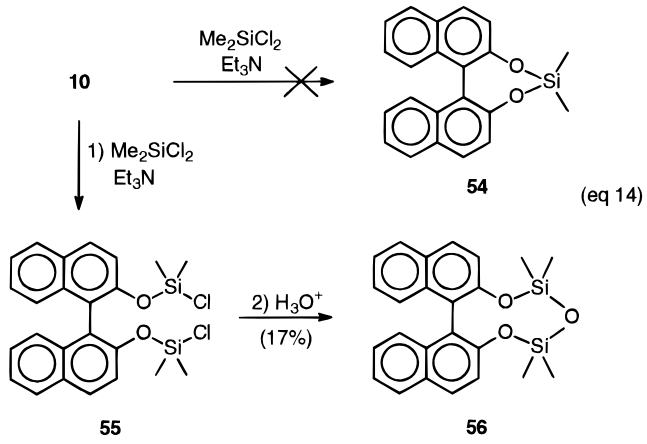
of oxygen from the MOM group to form the six-membered oxonium ion. The methylene protective group was also examined as shown in eq 13.



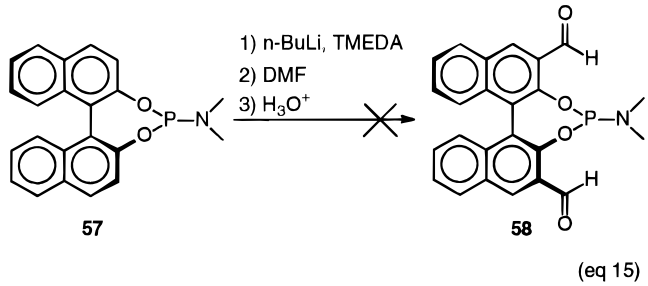
(13)

Methylene-protected derivative **51** is known,[39] but ortho-lithiation of this material turned out to be very difficult. The best result obtained even under forcing conditions was a mixture of monosubstituted **52** in 18% yield and the desired disubstituted **53** in 29% yield, which had to be separated by tedious column chromatography. The approach was abandoned. Apparently, the oxygen atoms in **51** are improperly oriented for stabilization of *o*-lithiums. Various attempts to prepare acetonides (acetone/acid, trimethyl orthoformate/acid) of **10** also failed.[40−42]

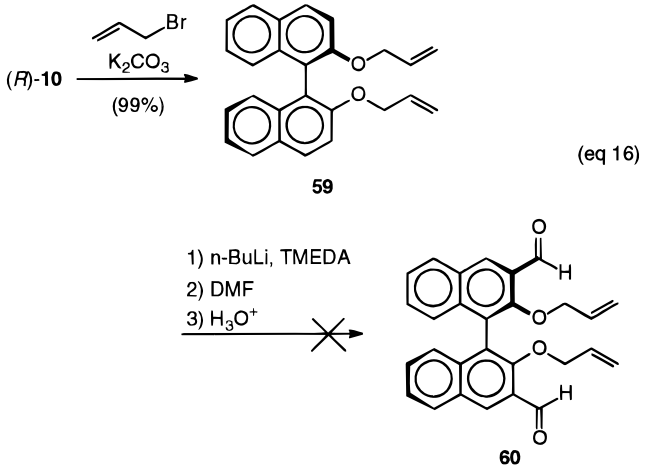
Several other protecting groups for **10** were examined. Protection of **10** with dichloro dimethylsilane[43,44] did not result in formation of the desired **54**, but of **56** (eq 14). Owing to the low yield of **56** together with the large size of its protective group[45] this compound was considered to be unsuitable for further exploration in the synthesis of thiocrown ethers of type **34**.



(eq 14)



(eq 15)



(eq 16)

Application of phosphepane **57**[46] (eq 15) and bis-allyl ether **59** (eq 16) as protected derivatives of **10** failed since both compounds were unstable under ortho-lithiation conditions. Bis-allyl derivative **59** seemed most promising since allyl groups have been successfully applied for protection of intraannular phenolic groups in oxocrown ethers.[36] Unfortunately, under the strongly basic conditions required for ortho-lithiation of **59** extensive rearrangement (not investigated further) occurs.

An alternative approach to thiocrown ethers bearing intraannular phenolic groups is by oxidative coupling of

(39) (a) Daub, G. H. *J. Org Chem.* **1973**, *38*, 1771. b)Tétreau, C.; Lavalette, D.; Cabaret, D.; Geraghty, N.; Welvart, Z. *J. Phys. Chem.* **1983**, *87*, 3234.
(40) Clode, D. M. *Chem. Rev.* **1979**, *79*, 491.
(41) Lipshutz, B. H.; Barton, J. C. *J. Org. Chem.* **1988**, *53*, 4495.
(42) Amarnath, V.; Broom, A. D. *Chem. Rev.* **1977**, *77*, 183.
(43) Furusawa, K. *Chem. Lett.* **1989**, 509.
(44) Trost, B. M.; Caldwell, C. G. *Tetrahedron Lett.* **1981**, *22*, 4999.
(45) We anticipated difficulties in the ring closing reaction when large substituents on the phenolic groups are present.
(46) (a) Hulst, A. J. R. L. Ph.D. Thesis, Groningen, the Netherlands, 1994, Chapter 3. (b) Van Basten, A.; Hulst, R.; Kellogg, R. M. *J. Chem. Soc., Perkin Trans. 1*, in press.

Scheme 3

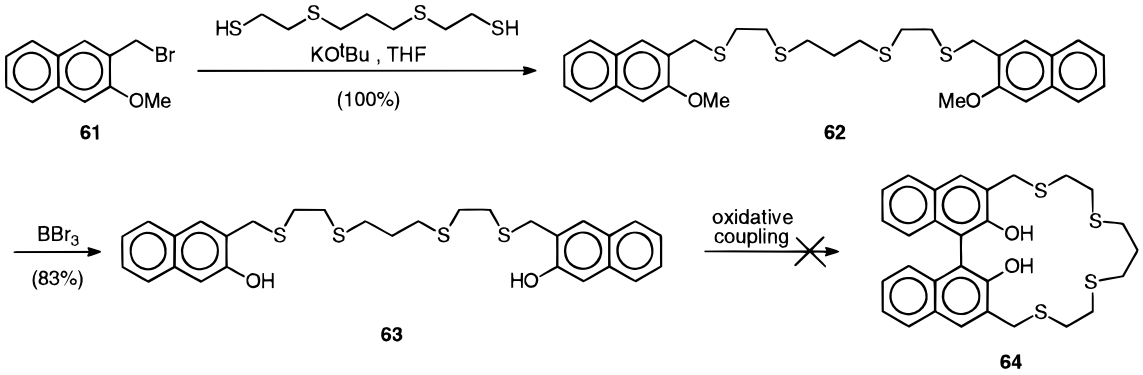


Table 2. Attempted Oxidative Phenol Coupling of 63

entry	oxidant	solvent	*T* (°C)	product(s)
1	$FeCl_3$[a]	water	100	starting material
2	$FeCl_3$[a]	MeOH/EtOH 1:2	reflux	starting material
3	$FeCl_3$[b]		50	starting material
4	$K_3Fe(CN)_6$[a]	MeOH	reflux	starting material
5	$Cu(II)(RNH_2)_4$[b]	MeOH	reflux	starting material
6	$-e^-$, 6.0 V	Bu_4NI/CH_3CN	16	polymeric material
7	$-e^-$, 3.5 V	KOH/water	19	polymeric material
8	$-e^-$, 4.0 V	KOH/MeOH	18	polymeric material
9	$-e^-$, 7.5 V	$NiCl_2$/MeOH	23	polymeric material

[a] 1.1 equiv of oxidant. [b] 2 equiv of oxidant.

two naphthol units already bearing the thiocrown ether chain. One such attempt is outlined in eq 17 (Scheme 3).

Starting material **61** was prepared by known procedures[47] and was readily converted to **63** in two steps. Oxidative cyclization of **63** to (racemic) **64** failed under all conditions examined. The results are summarized in Table 2.

Reaction of **63** with oxidants, like $FeCl_3$,[48] $K_3Fe(CN)_6$,[49] and $Cu(II)(RNH_2)_4$,[50] known to couple efficiently 2-naphthol to 1,1′-binaphthalene-2,2′-diol, failed to effect coupling to give **64** (Table 2, entries 1−5). In all these attempts only starting material was recovered. Our hopes that transition metals like Fe(III) would act both as oxidant and template were unfortunately not rewarded. Attempts to accomplish coupling via electrochemical oxidation[51] also failed; all attempts resulted in formation of polymeric material (Table 2, entries 6−9).

In view of the number of unsuccessful efforts to synthesize thiocrown ethers containing intraannular phenolic groups we gave up further attempts to prepare these compounds.

Conclusion

The syntheses of two types of new and enantiomerically pure thiocrown ethers derived from 1,1′-binaphthalene-2,2′-diol have been achieved. These enantiomerically pure thiocrown ethers are being investigated as ligands in asymmetric catalysis.[17,52] This work will be reported in due course.

Experimental Section

General Remarks. All reactions were performed in a nitrogen atmosphere, unless otherwise stated. Melting points are uncorrected. Optical rotations were measured at room temperature (20 °C) at the sodium D line (589 nm) and at the mercury lines (578, 546, 436, 365 nm). ^{1}H NMR spectra were recorded at 60, 200, or 300 MHz. ^{13}C NMR spectra were recorded at 50.3 or 75.4 MHz. Mass spectra were recorded by Mr. A. Kiewiet. Elemental analyses were performed in the Microanalytical Department of this laboratory by Mr. H. Draayer, J. Ebels, J. Hommes, and J. E. Vos. All solvents and reagents were purified and dried, following standard procedures.[53] Reagents were purchased from Janssen Chimica, Aldrich Chemical Co., and Fluka. 1,1′-Binaphthalene-2,2′-diol (**10**) was purchased from Syncom BV. 1,4,7-Trithiaheptane was purchased from Aldrich Chemical Co. Compounds **36**,[27] **39**,[27] **51**,[39] **61**,[47] and dithiols 1,5,9-trithianonane,[54] 1,4,7,10-tetrathiadecane,[55] 1,4,8,11-tetrathiaundecane,[8b] 1,5,10,14-tetrathiatetradecane,[55] 2-(mercaptomethyl)-1-propene-3-thiol,[56] 1,2-benzenedithiol,[57] 1,2-bis(mercaptomethyl)benzene,[58] and 2,2-dimethyl-1,3-propanedithiol[56,59] were prepared according to literature procedures. Compound **57**[46] was kindly donated by Dr. R. Hulst. In some substitution reactions 4-(*N*,*N*-

(47) (a) Yamamoto, K.; Fukushima, H.; Yumioka, H.; Nakazaki, M. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3633. (b) Huisgen, R.; Nakaten, H. *Liebegs Ann. Chem.* **1954**, *586*, 84. (c) Werner, A.; Seybold, W. *Ber. Deutsch. Chem. Ges.* **1904**, *37*, 3661.

(48) (a) Pummerer, R.; Prell, E.; Rieche, A. *Chem. Ber.* **1926**, *59*, 2159. (b) Toda, F.; Tanaka, K.; Iwata, S. *J. Org. Chem.* **1989**, *54*, 3007.

(49) McDonald, P. D.; Hamilton, G. A. Mechanisms of Phenolic Oxidative Coupling Reactions. In *Oxidation in Organic Chemistry*; Trahanovsky, W. S. Ed.; Academic Press: New York, 1973.

(50) (a) Brussee, J.; Groenendijk, J. L. G.; Te Koppele, J. M.; Jansen, A. C. A. *Tetrahedron* **1985**, *41*, 3313. (b) Feringa, B.; Wynberg, H. *Bioorg. Chem.* **1978**, *7*, 397.

(51) (a) Kashiwagi, Y.; Ono, H.; Osa, T. *Chem. Lett.* **1993**, 81. (b) Zweig, A.; Maurer, A. H.; Roberts, B. G. *J. Org. Chem.* **1967**, *32*, 1322. (c) Papouchado, L.; Sandford, R. W.; Petrie, G.; Adams, R. N. *J. Electroanal. Chem.* **1975**, *65*, 275.

(52) Thiocrown ethers **26** and **42** have been tested as ligands in Ni-(II)-catalyzed conjugate addition reactions: De Vries, A. H. M.; Jansen, J. F. G. A.; Feringa, B. L. *Tetrahedron* **1994**, *50*, 4479.

(53) *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Longman: London, 1978.

(54) Setzer, W. N.; Afshar, S.; Burns, N. L.; Ferrante, L. A.; Hester, A. M.; Meehan Jr., E. J.; Grant, G. J.; Isaac, S. M.; Laudeman, C. P.; Lewis, C. M.; VanDerveer, D. G. *Heteroatom. Chem.* **1990**, *1*, 375.

(55) Wolf, R. E., Jr.; Hartman, J.-A. R.; Storey, J. M. E.; Foxman, B. M.; Cooper, S. R. *J. Am. Chem. Soc.* **1987**, *109*, 4328.

(56) Houk, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1987**, *109*, 6825.

(57) Giolando, D. M.; Kirschbaum, K. *Synthesis* **1992**, 451.

(58) Mayerle, J. J.; Denmark, S. E.; DePamphilis, B. V.; Ibers, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1975**, *97*, 1032.

(59) Eliel, E. L.; Rao, V. S.; Smith, S.; Hutchins, R. O. *J. Org. Chem.* **1975**, *40*, 524.

dimethylamino)pyridine (DMAP) was added as hypernucleophilic catalyst.[60]

2,2′-Diethoxy-1,1′-binaphthyl (12).[61] **Optimized Reaction Conditions.**[17] A solution of (*R*)-**10** (286 mg, 1.00 mmol), K_2CO_3 (0.41 g, 3.0 mmol), and ethyl bromide (0.30 mL, 4.0 mmol) in DMF (15 mL) was stirred at 110 °C for 24 h. The reaction mixture was cooled to rt, filtered, and concentrated under reduced pressure to give a white solid (330 mg). The crude product was filtered over a short silica gel column (CH_2Cl_2) to give **12** (100%): mp 135.1−136.2 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.10 (t, J = 7.0 Hz, 6 H), 4.09 (q, J = 7.0 Hz, 4 H), 7.17−7.49 (m, 8 H), 7.90 (d, J = 7.9 Hz, 2 H), 7.98 (d, J = 9.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 15.0 (q), 65.2 (t), 115.9 (d), 120.7 (s), 123.4 (d), 125.5 (d), 126.1 (d), 127.8 (d), 129.1 (d), 129.3 (s), 134.2 (s), 154.3 (s); ee 99.6%, as determined by HPLC.[62]

(*R*)-(−)-2,2′-Bis(2-hydroxyethoxy)-1,1′-binaphthyl (13). The literature procedure for preparation of the (*S*)-enantiomer[16] was improved and applied for preparation of both (*R*)- and (*S*)-**13**: (*R*)-(+)-**10** (8.62 g, 30.1 mmol), 2-chloroethanol (8.0 mL, 119 mmol), and K_2CO_3 (16.6 g, 120 mmol) were dissolved in DMF (250 mL) and stirred at 110 °C for 17 h. The reaction mixture was filtrated and concentrated under reduced pressure. The residue was taken up in CH_2Cl_2 (150 mL) and washed with water (2 × 100 mL) and 2 N NaOH (100 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give a pale yellow oil (12.15 g). The crude product was purified by column chromatography (silica gel, Et_2O) giving **13** (77%) as a white foam: mp 130−134 °C; $[\alpha]_{578}$ = −26.4 (c = 0.762, THF), $[\alpha]_{546}$ = −26.6; $[\alpha]_{436}$ = +14.0; $[\alpha]_{365}$ = +543.8; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.42 (s, br, 2 H), 3.45−3.70 (m, br, 4 H), 3.98−4.07 (m, 2 H), 4.18−4.28 (m, 2 H), 7.13−7.48 (m, 8 H), 7.91 (d, J = 7.3 Hz, 2 H), 8.00 (d, J = 9.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 61.2 (t), 71.7 (d), 115.9 (d), 120.3 (s), 124.1 (d), 125.2 (d), 126.7 (d), 128.2 (d), 129.6 (s), 129.8 (d), 133.8 (s), 153.5 (s); HRMS m/e (M^+) calcd 374.152, obsd 374.152.

(*S*)-(+)-13.[16] By the same procedure (*S*)-**13** (71%) was obtained: mp 131−134 °C; $[\alpha]_{578}$ = +25.1 (c = 0.958, THF), $[\alpha]_{546}$ = +25.4 (lit.[16] $[\alpha]_{546}$ = +23.2 (c = 1.05, THF)); $[\alpha]_{436}$ = −13.4; $[\alpha]_{365}$ = +522.6.

(*R*)-(−)-2,2′-Bis(2-(mesyloxy)ethoxy)-1,1′-binaphthyl (14). To a solution of (*R*)-**13** (1.87 g, 5.0 mmol), triethylamine (1.5 mL, 11 mmol), and DMAP (20 mg, 0.16 mmol) in CH_2Cl_2 (75 mL) was dropwise added methanesulfonyl chloride (0.85 mL, 11.0 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 17 h and subsequently washed with water (2 × 50 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give a viscous, slightly yellow oil (2.80 g). The crude product was crystallized from toluene/*n*-hexane to give **14** (95%) as white crystals: mp 143−144 °C; $[\alpha]_{578}$ = −30.5 (c = 0.650, THF); $[\alpha]_{546}$ = −32.8; $[\alpha]_{436}$ = −24.3; $[\alpha]_{365}$ = +237; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.83 (s, 6 H), 3.93−4.11 (m, 8 H), 6.90−7.25 (m, 8 H), 7.66−7.71 (m, 2 H), 7.77−7.82 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 35.9 (q), 67.0 (t), 68.7 (t), 114.8 (d), 119.7 (s), 124.1 (d), 125.0 (d), 126.7 (d), 127.8 (d), 129.3 (s), 129.6 (d), 133.7 (s), 153.2 (s); HRMS m/e (M^+) calcd 530.107, obsd 530.106. Anal. Calcd (found) for $C_{26}H_{26}O_8S_2$: C, 58.85 (58.67); H, 4.94 (5.03); S, 12.09 (11.98).

(*S*)-(+)-14. By the same procedure (*S*)-**14** (92%) was obtained: mp 142−143 °C; $[\alpha]_{578}$ = +30.4 (c = 0.834, THF); $[\alpha]_{546}$ = +32.6; $[\alpha]_{436}$ = +24.4; $[\alpha]_{365}$ = −234.

(*R*)-(+)-2,2′-Bis(3-hydroxypropoxy)-1,1′-binaphthyl (15) and (*R*)-(+)-2-(3-Hydroxypropoxy)-2′-hydroxy-1,1′-binaphthyl (16). (*R*)-15 and (*R*)-16 by alkylation of (*R*)-(+)-10. (*R*)-(+)-**10** (10.0 g, 35.0 mmol), 3-chloro-1-propanol (13.2 g, 100 mmol) and K_2CO_3 (19.4 g, 140 mmol) were dissolved in DMF (250 mL) and stirred at 110 °C for 17 h. The reaction mixture was filtered and concentrated under reduced pressure. The residue was taken up in CH_2Cl_2 (300 mL) and washed with water (100 mL) and 4 N NaOH (2 × 150 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give a pale yellow oil (21.05 g). The oil was heated in a bulb to bulb distillation apparatus (0.1 mmHg, 225 °C) to remove dimeric byproduct **17**. The residue of distillation (16.25 g) was purified by column chromatography (silica gel, Et_2O) to give the mono-alkylated product (**16**, 21%). Further elution (EtOAc) gave **15** (59%) as a white foam.

Compound **16**: mp 179.6−181.0 °C; $[\alpha]_{578}$ = +30.4 (c = 0.938, THF), $[\alpha]_{546}$ = +39.6, $[\alpha]_{436}$ = +152.5, $[\alpha]_{365}$ = +843.4; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.65−1.71 (m, 2 H), 1.95 (s, br, 1 H), 3.28−3.30 (m, 2 H), 4.08−4.15 (m, 2 H), 5.94 (s, br, 1 H), 7.16 (d, J = 8.8 Hz, 1 H), 7.27−7.47 (m, 7 H), 7.92−7.96 (m, 3 H), 8.04 (d, J = 9.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 31.3 (t), 59.7 (t), 67.2 (t), 114.9 (d), 116.8 (s), 117.5 (d), 123.1 (d), 124.0 (d), 124.5 (d), 124.9 (d), 126.2 (d), 126.9 (d), 127.9 (d), 128.0 (d), 128.8 (s), 129.3 (s), 129.6 (d), 130.4 (d), 133.6 (s), 133.8 (s), 151.1 (s), 154.7 (s); HRMS m/e (M^+) calcd 344.141, obsd 344.142.

Compound **15**: mp 66.3−68.3 °C; $[\alpha]_{589}$ = +41.0 (c = 0.442, THF), $[\alpha]_{578}$ = +50.2, $[\alpha]_{546}$ = +60.9, $[\alpha]_{436}$ = +172.0, $[\alpha]_{365}$ = +716.1; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.56−1.80 (m, 4 H), 2.06 (s, br, 2 H), 3.29−3.31 (m, br, 4 H), 4.02−4.27 (m, 4 H), 7.13−7.49 (m, 8 H), 7.90 (d, J = 7.7 Hz, 2 H), 8.00 (d, J = 9.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 31.5 (t), 60.1 (t), 67.6 (t), 114.8 (d), 119.7 (s), 123.7 (d), 125.1 (d), 126.3 (d), 127.9 (d), 129.3 (s), 129.5 (d), 133.7 (s), 153.7 (s); HRMS m/e (M^+) calcd 402.183, obsd 402.183.

(*S*)-15 by Hydrolysis of (*aS*)-19. To a stirred solution of (*aS*)-**19** (10.18 g, 17.9 mmol) in acetone (200 mL) at rt was added 6 N HCl (23 mL, 138 mmol). After 17 h the reaction mixture was neutralized with Na_2CO_3 and concentrated under reduced pressure. The residue was taken up in CH_2Cl_2 (300 mL) and washed with water (2 × 150 mL) and 0.5 N NaOH (100 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give a yellow foam (7.14 g). The crude product was purified by column chromatography (silica gel, EtOAc) to give **15** (95%) as a white foam: mp 66.7−68.2 °C; $[\alpha]_D$ = −40.8 (c = 0.526, THF), $[\alpha]_{578}$ = −49.7, $[\alpha]_{546}$ = −60.4, $[\alpha]_{436}$ = −170.7, $[\alpha]_{365}$ = −709.2. The NMR data were in accord with the data for the product obtained from **10** (vide supra).

(*aS*)-2,2′-Bis(3-(pyranyl-2-oxy)propoxy)-1,1′-binaphthyl (19). (*S*)-(−)-**10** (5.72 g, 20.0 mmol), 2-(3-chloro-1-propoxy)pyran[63] (7.50 g, 42.0 mmol), and K_2CO_3 (5.80 g, 42 mmol) were dissolved in DMF (150 mL) and stirred at 110 °C for 4 h. The reaction mixture was concentrated under reduced pressure, and the residue was taken up in CH_2Cl_2 (200 mL) and washed with water (2 × 150 mL), 2 N NaOH (2 × 150 mL), and brine (150 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil (10.61 g). The crude product was purified by column chromatography (silica gel, Et_2O) to give **19** (89%) as a yellow oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.38−1.78 (m, 16 H), 2.87−3.06 (m, 2 H), 3.33- 3.45 (m, 4 H), 3.65−3.75 (m, 2 H), 4.03−4.16 (m, 5 H), 4.28−4.31 (m, 1 H), 7.15−7.47 (m, 8 H), 7.88 (d, J = 8.1 Hz, 2 H), 7.96 (d, J = 9.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 19.4 (t), 19.6 (t), 25.3 (t), 29.5 (t), 29.6 (t), 30.4 (t), 61.9 (t), 62.0 (t), 62.1 (t), 63.6 (t), 63.7 (t), 63.8 (t), 66.2 (t), 66.3 (t), 66.4 (t), 98.6 (d), 98.7 (d), 115.4 (d), 120.2 (s), 120.3 (s), 123.2 (d), 123.3 (d), 125.2 (d), 125.2 (d), 125.9 (d), 127.6 (d), 127.6 (d), 128.9 (d), 129.0 (s), 133.9 (s), 154.0 (s), 154.1 (s); HRMS m/e (M^+) calcd 570.298, obsd 570.298.

2,2′-Bis(3-bromopropoxy)-1,1′-binaphthyl (20). (*S*)-20 From 19. Triphenylphosphine (21.2 g, 81 mmol) was dissolved in CH_2Cl_2 (150 mL) and cooled to 0 °C. Bromine (4.14 mL, 81 mmol) was slowly added, initially forming a white precipitate that turns orange upon further adding. After all the bromine had been added the reaction mixture was stirred at 0 °C for

(60) (a) Scriven, E. F. V. *Chem. Soc. Rev.* **1983**, *13*, 129. (b) Höfle, G.; Steglich, W.; Vorbrüggen, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 569.

(61) Zinke, A.; Dengg, R. *Monatsh. Chem.* **1922**, *43*, 127.

(62) A water-cooled 250 × 4.6 mm (+)-poly(triphenylmethyl methacrylate) column (DAICEL OT$^+$) was used, with *n*-hexane/2-propanol 100:1 as eluent (flow 0.5 mL/min); retention times: (*S*)-**12**, 34.76 min; (*R*)-**12**, 42.95 min. (a) Okamoto, Y.; Honda, S.; Okamoto, I.; Yuki, K.; Murata, S.; Noyori, R.; Takaya, H. *J. Am. Chem. Soc.* **1981**, *103*, 6971. (b) Okamoto, Y.; Hatada, K. *J. Liq. Chromatogr.* **1986**, *9*, 369.

(63) Parham, W. E.; Anderson, E. L. *J. Am. Chem. Soc.* **1948**, *70*, 4187.

45 min. A solution of **19** (8.6 g, 15.1 mmol) in CH_2Cl_2 (30 mL) was added in 15 min at 0 °C, and the reaction mixture was stirred at room temperature for 17 h. CH_2Cl_2 (100 mL) was added, and the reaction mixture was washed twice with water. The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give a light brown solid (22.3 g). The solid was recrystallized from toluene/*n*-octane to give white crystals (7.28 g, triphenylphosphine oxide). The mother liquor was concentrated under reduced pressure and purified by column chromatography (silica gel, CH_2Cl_2/*n*-hexane 1:1) to give a yellowish brown oil (7.00 g). This oil was boiled in methanol and decanted while hot. The decantate was concentrated under reduced pressure to give **20** (73%) as a yellow oil. Analytically pure material was obtained by additional column chromatography (silica gel, toluene) to give **20** as a colorless oil: $[\alpha]_D = -46.5$ ($c = 0.400$, THF), $[\alpha]_{578} = -49.8$, $[\alpha]_{546} = -59.8$, $[\alpha]_{436} = -145.5$, $[\alpha]_{365} = -442.0$; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.92−1.99 (m, 4 H), 2.84−3.02 (m, 4 H), 4.06−4.20 (m, 4 H), 7.22−7.48 (m, 8 H), 7.92 (d, $J = 8.1$ Hz, 2 H), 8.00 (d, $J = 9.2$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 30.0 (t), 32.4 (t), 66.8 (t), 115.3 (d), 120.3 (s), 123.6 (d), 125.2 (d), 126.3 (d), 127.7 (d), 129.2 (s), 129.3 (d), 133.8 (s), 153.7 (s); HRMS *m*/*e* (M^+) calcd 526.014, obsd 526.013. Anal. Calcd (found) for $C_{26}H_{24}O_2Br_2$: C, 59.11 (59.19); H, 4.58 (4.58); Br, 30.25 (30.15).

(*R*)-20 from 15. Compound **15** (7.93 g, 19.7 mmol) was dissolved in THF (150 mL). Pyridine (0.61 mL, 7.5 mmol) was added, and the reaction mixture was cooled to 0 °C. Phosphorus tribromide (2.0 mL, 21.3 mmol) was added in 5 min, giving a white precipitate. The reaction mixture was allowed to warm to room temperature. After being stirred at ambient temperature for 20 h the reaction mixture was concentrated under reduced pressure. The residue was taken up in benzene (100 mL) and water (150 mL). The benzene layer was separated, and the water layer was extracted with benzene (2 × 75 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to give a yellow oil (16.17 g). The crude product was purified by column chromatography (silica gel, toluene) to give **20** (19%) as a colorless oil: $[\alpha]_D = +46.0$ ($c = 0.544$, THF), $[\alpha]_{578} = +49.1$, $[\alpha]_{546} = +58.9$, $[\alpha]_{436} = +144.0$, $[\alpha]_{365} = +436.9$; ^{1}H NMR and ^{13}C NMR spectra were identical to the spectra of (*S*)-**20** obtained from **19**.

(*R*)-(+)-2,2′-Bis(2-bromoethoxy)-1,1′-binaphthyl (21). A solution of (*R*)-**14** (2.43 g, 4.58 mmol) and anhydrous lithium bromide (1.20 g, 13.8 mmol) in DMSO (40 mL) was stirred at 60 °C for 20 h. Water (50 mL) was added, and the mixture was extracted with Et_2O (3 × 50 mL). The combined Et_2O layers were washed with brine (75 mL), dried ($MgSO_4$), and concentrated under reduced pressure to give a yellow oil (2.25 g). The crude product was purified by column chromatography (silica gel, CH_2Cl_2) to give **21** (94%) as colorless crystals. Recrystallization from CH_2Cl_2/*n*-hexane afforded very long needles: mp 91.2−92.4 °C; $[\alpha]_D = +45.6$ ($c = 0.296$, THF), $[\alpha]_{578} = +50.3$, $[\alpha]_{546} = +59.8$, $[\alpha]_{436} = +150.0$, $[\alpha]_{365} = +552.4$; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.31 (t, $J = 6.6$ Hz, 4 H), 4.21−4.42 (m, 4 H), 7.26; ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 29.5 (t), 70.0 (t), 116.4 (d), 121.1 (s), 124.3 (d), 125.5 (d), 126.7 (d), 128.1 (d), 129.8 (d), 129.9 (s), 134.1 (s), 153.7 (s); HRMS *m*/*e* (M^+) calcd 497.983, obsd 497.983.

(*S*)-(−)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-9,13-dithiacyclopentadeca-2,4-diene (22). Typical Procedure. A solution of (*S*)-**14** (2.65 g, 5.0 mmol) and 1,3-propanedithiol (0.51 g, 5.1 mmol) in DMF (150 mL) was added dropwise to a stirred suspension of Cs_2CO_3 (3.43 g, 10.5 mmol) in DMF (600 mL) at 60 °C over a period of 10−18 h. The reaction mixture was filtered and concentrated under reduced pressure. The residue was taken up in CH_2Cl_2 (100 mL) and washed with water (2 × 100 mL) and 2 N NaOH (2 × 100 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give a yellow foam (2.64 g). The crude product was purified by column chromatography (silica gel, toluene) to give **22** (30%) as a white foam: mp 64.2−64.6 °C; $[\alpha]_{578} = -201.9$ ($c = 1.054$, THF), $[\alpha]_{546} = -238.4$, $[\alpha]_{436} = -530.8$, $[\alpha]_{365} = -1596$; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.73−1.88 (m, 2 H), 2.44−2.68 (m, 8 H), 4.08−4.20 (m, 4 H), 7.15−7.47 (m, 8 H), 7.89 (d, $J = 7.7$ Hz, 2 H), 7.98 (d, $J = 8.8$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ 30.0 (t), 30.3 (t), 31.2 (t), 70.5 (t), 116.8 (d), 121.2 (s), 123.8 (d), 125.3 (d), 126.2 (d), 127.8 (d), 129.3 (d), 129.6 (s), 133.9 (s), 154.1 (s); HRMS *m*/*e* (M^+) calcd 446.137, obsd 446.136.

(*R*)-22 from (R)-21 and 1,3-Propanedithiol. Reaction of (*R*)-**21** (500 mg, 1.00 mmol) and 1,3-propanedithiol (100 mg, 1.00 mmol) afforded (*R*)-**22** in 31% yield: mp 64.3−64.6 °C; $[\alpha]_{578} = +204.8$ ($c = 0.968$, THF), $[\alpha]_{546} = +242.0$, $[\alpha]_{436} = +538.0$, $[\alpha]_{365} = +1624$.

(*S*)-(−)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-9,12-dithiacyclotetradeca-2,4-diene (23). According to the procedure described for the synthesis of **22**, from (*S*)-**14** and 1,2-ethanedithiol: yield 32%; mp 75.7−76.2 °C; $[\alpha]_{578} = -153.5$ ($c = 0.998$, THF), $[\alpha]_{546} = -183.0$, $[\alpha]_{436} = -444.6$, $[\alpha]_{365} = -1576$; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.47−2.88 (m, 8 H), 4.06−4.41 (m, 4 H), 7.12−7.53 (m, 8 H), 7.90 (d, $J = 8.1$ Hz, 2 H), 7.99 (d, $J = 8.8$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 30.2 (t), 31.5 (t), 72.3 (t), 117.3 (d), 121.3 (s), 124.0 (d), 125.1 (d), 126.3 (d), 127.8 (d), 129.4 (d), 129.7 (s), 133.8 (s), 153.9 (s); HRMS *m*/*e* (M^+) calcd 432.122, obsd 432.122.

(*R*)-(+)-23: yield 30%; mp 74.8−75.9 °C; $[\alpha]_{578} = +156.6$ ($c = 0.554$, THF), $[\alpha]_{546} = +186.4$, $[\alpha]_{436} = +455.0$, $[\alpha]_{365} = +1612$.

(*R*)-23 from (*R*)-21 and 1,2-ethanedithiol: yield 33%; mp 75.4−76.4 °C; $[\alpha]_{578} = +156.0$ ($c = 0.660$, THF), $[\alpha]_{546} = +186.1$, $[\alpha]_{436} = +455.1$, $[\alpha]_{365} = +1608$.

(*R*)-(+)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-9,12,15-trithiacycloheptadeca-2,4-diene (24). According to the procedure described for the synthesis of **22**, from (*R*)-**14** and 1,4,7-trithiaheptane: yield 58%; mp 54.3−56.1 °C; $[\alpha]_{578} = +90.7$ ($c = 1.060$, THF), $[\alpha]_{546} = +109.6$, $[\alpha]_{436} = +283.8$, $[\alpha]_{365} = +1065$; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.28−2.97 (m, 12 H), 3.85−4.02 (m, 4 H), 6.97−7.32 (m, 8 H), 7.72 (d, $J = 8.0$ Hz, 2 H), 7.81 (d, $J = 8.8$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 30.9 (t), 31.2 (t), 32.2 (t), 71.4 (t), 116.6 (d), 121.0 (s), 123.9 (d), 125.3 (d), 126.3 (d), 127.8 (d), 129.5 (d), 129.6 (s), 133.9 (s), 153.9 (s); HRMS *m*/*e* (M^+) calcd 492.125, obsd 492.126. Anal. Calcd (found) for $C_{28}H_{28}O_2S_3$: C, 68.26 (67.83); H, 5.73 (5.69); S, 19.52 (19.24).

(*S*)-24 from (*S*)-14 and 1,4,7-trithiaheptane: yield 52%; mp 54.8−56.1 °C; $[\alpha]_{578} = -91.7$ ($c = 0.542$, THF), $[\alpha]_{546} = -110.6$, $[\alpha]_{436} = -287.2$, $[\alpha]_{365} = -1081$; ee > 99.5% as determined by HPLC.[64]

(*R*)-(+)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-9,12,16,19-tetrathiacyclouneicosa-2,4-diene (25). According to the procedure described for the synthesis of **22**, from (*R*)-**14** and 1,4,8,11-tetrathiaundecane: yield 54% as a colorless oil; $[\alpha]_D = +130.3$ ($c = 0.284$, THF), $[\alpha]_{578} = +141.9$, $[\alpha]_{546} = +168.0$, $[\alpha]_{436} = +376.1$, $[\alpha]_{365} = +1081$; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.86 (quintet, $J = 6.8$ Hz, 2 H), 2.39−2.74 (m, 16 H), 4.05−4.35 (m, 4 H), 7.16−7.50 (m, 8 H), 7.90 (d, $J = 7.8$ Hz, 2 H), 8.00 (d, $J = 9.0$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 29.8 (t), 30.6 (t), 31.2 (t), 32.4 (t), 32.5 (t), 70.5 (t), 115.7 (d), 120.7 (s), 124.0 (d), 125.4 (d), 126.5 (d), 127.9 (d), 129.6 (d), 134.1 (s), 153.9 (s); HRMS *m*/*e* (M^+) calcd 566.144, obsd 566.144.

(*S*)-(−)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-10,14-dithiacycloheptadeca-2,4-diene (26). According to the procedure described for the synthesis of **22**, from (*S*)-**20** and 1,3-propanedithiol: yield 61%; mp 107.6−109.9 °C; $[\alpha]_{578} = -163.7$ ($c = 1.098$, THF), $[\alpha]_{546} = -193.8$, $[\alpha]_{436} = -446.2$, $[\alpha]_{365} = -1433$; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.69−1.78 (m, 6 H), 2.25−2.40 (m, 4 H), 2.53 (t, $J = 7.0$ Hz, 4 H), 3.83−3.90 (m, 2 H), 4.27−4.34 (m, 2 H), 7.10−7.47 (m, 8 H), 7.88 (d, $J = 8.0$ Hz, 2 H), 7.96 (d, $J = 8.8$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 27.6 (t), 29.3 (t), 29.6 (t), 30.4 (t), 67.5 (t), 115.5 (d), 120.4 (s), 123.4 (d), 125.2 (d), 126.1 (d), 127.7 (d), 129.1 (d), 129.2 (s), 134.0 (s), 154.1 (s); HRMS *m*/*e* (M^+) calcd 474.169, obsd 474.169.

(*S*)-(−)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-10,14,18-trithiacyclouneicosa-2,4-diene (27). According to the procedure described for the synthesis of **22**, from (*S*)-**20** and 1,5,9-trithianonane: yield 47% as a colorless oil; $[\alpha]_D = -130.7$ (*c*

(64) A water-cooled DAICEL OT$^+$ column was used, with *n*-hexane/2-propanol 9:1 as eluent (flow 1.0 mL/min); a solution of **24** in 2-propanol was injected; retention times: (*S*)-**24**, 28.3 min; (*R*)-**24**, 48.0 min.

= 0.668, THF), $[\alpha]_{578}$ = −142.2, $[\alpha]_{546}$ = −167.4, $[\alpha]_{436}$ = −368.1, $[\alpha]_{365}$ = −1060; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.73−1.94 (m, 8 H), 2.32 (t, J = 7.1 Hz, 4 H), 2.48−2.63 (m, 4 H), 2.68 (t, J = 7.1 Hz, 4 H), 3.97−4.07 (m, 2 H), 4.19−4.30 (m, 2 H), 7.22−7.45 (m, 6 H), 7.54 (d, J = 9.0 Hz, 2 H), 7.96 (d, J = 7.8 Hz, 2 H), 8.04 (d, J = 9.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 28.3 (t), 29.4 (t), 29.7 (t), 30.3 (t), 30.8 (t), 68.0 (t), 115.8 (d), 120.6 (s), 123.7 (d), 125.5 (d), 126.4 (d), 128.0 (d), 129.4 (d), 129.5 (s), 134.2 (s), 154.3 (s); HRMS *m*/*e* (M^+) calcd 548.188, obsd 548.188.

(*R*)-(+)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-9,13-dithia-11,11-dimethylcyclotetradeca-2,4-diene (28). According to the procedure described for the synthesis of **22**, from (*R*)-**14** and 2,2-dimethyl-1,3-propanedithiol: yield 37%; mp 89.2−89.9 °C; $[\alpha]_D$ = +257.6 (*c* = 0.304, THF), $[\alpha]_{578}$ = +286.2, $[\alpha]_{546}$ = +335.2, $[\alpha]_{436}$ = +716.1, $[\alpha]_{365}$ = +1981; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.05 (s, 6 H), 2.36 (d, J = 12.6 Hz, 2 H), 2.48−2.60 (m, 2 H), 2.78 (d, J = 12.6 Hz, 2 H), 2.71−2.96 (m, 2 H), 4.12−4.30 (m, 4 H), 7.21−7.50 (m, 8 H), 7.93 (d, J = 7.7 Hz, 2 H), 8.02 (d, J = 9.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 27.8 (q), 31.6 (t), 36.4 (s), 41.1 (t), 68.0 (t), 115.7 (d), 123.7 (d), 125.5 (d), 126.4 (d), 128.0 (d), 128.0 (s), 129.4 (d), 134.2 (s), 153.8 (s); HRMS *m*/*e* (M^+) calcd 474.169, obsd 474.169.

(*S*)-(−)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-10,14-dithia-12,12-dimethylcycloheptadeca-2,4-diene (29). According to the procedure described for the synthesis of **22**, from (*S*)-**20** and 2,2-dimethyl-1,3-propanedithiol: yield 24%; mp 174.6−176.6 °C; $[\alpha]_D$ = −145.3 (*c* = 0.298, THF), $[\alpha]_{578}$ = −159.7, $[\alpha]_{546}$ = −189.3, $[\alpha]_{436}$ = −434.6, $[\alpha]_{365}$ = −1427; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.03 (s, 6 H), 1.72−1.85 (m, 4 H), 2.34−2.72 (m, 8 H), 3.88−3.98 (m, 2 H), 4.22−4.34 (m, 2 H), 7.13−7.39 (m, 6 H), 7.47 (d, J = 8.9 Hz, 2 H), 7.90 (d, J = 7.7 Hz, 2 H), 7.98 (d, J = 8.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 27.6 (q), 29.3 (t), 29.5 (t), 35.9 (s), 42.9 (t), 67.4 (t), 115.2 (d), 120.2 (s), 123.4 (d), 125.3 (d), 126.2 (d), 127.9 (d), 129.1 (s), 129.2 (d), 134.1 (s), 154.2 (s); HRMS *m*/*e* (M^+) calcd 502.200, obsd 502.200.

(*S*)-(−)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-9,13-dithia-11-methylenecyclopentadeca-2,4-diene (30). According to the procedure described for the synthesis of **22**, from (*S*)-**14** and 2-(mercaptomethyl)-1-propene-3-thiol: yield 20%; mp 54.5−55.6 °C; $[\alpha]_{578}$ = −176.6 (*c* = 0.988, THF), $[\alpha]_{546}$ = −208.8, $[\alpha]_{436}$ = −468.6, $[\alpha]_{365}$ = −1423; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.55−2.68 (m, 4 H), 3.28 (AB system, J_1 = 62.6 Hz, J_2 = 13.9 Hz, 4 H), 4.15−4.31 (m, 4 H), 5.08 (s, 2 H), 7.17−7.43 (m, 8 H), 7.91 (d, J = 8.1 Hz, 2 H), 7.99 (d, J = 9.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 31.4 (t), 36.4 (t), 69.3 (t), 114.8 (t), 115.1 (d), 120.2 (s), 123.5 (d), 125.2 (d), 126.2 (d), 127.8 (d), 129.2 (d), 134.0 (s), 142.6 (s), 153.8 (s); HRMS *m*/*e* (M^+) calcd 458.137, obsd 458.136.

(*S*)-(−)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-10,14-dithia-12-methylenecycloheptadeca-2,4-diene (31). According to the procedure described for the synthesis of **22**, from (*S*)-**20** and 2-(mercaptomethyl)-1-propene-3-thiol: yield 68%; mp 69.8−70.4 °C; $[\alpha]_{578}$ = −138.5 (*c* = 0.960, THF), $[\alpha]_{546}$ = −165.6, $[\alpha]_{436}$ = −399.1, $[\alpha]_{365}$ = −1377; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.72−1.87 (m, 4 H), 2.23−2.45 (m, 4 H), 3.22 (AB system, J_1 = 24.0 Hz, J_2 = 14.5 Hz, 4 H), 3.86−3.93 (m, 2 H), 4.20−4.27 (m, 2 H), 5.04 (s, 2 H), 7.09−7.45 (m, 8 H), 7.87 (d, J = 8.1 Hz, 2 H), 7.96 (d, J = 9.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 28.5 (t), 29.2 (t), 36.2 (t), 67.7 (t), 114.8 (t), 115.2 (d), 120.1 (s), 123.4 (d), 125.1 (d), 126.1 (d), 127.7 (d), 129.0 (d), 129.1 (s), 134.0 (s), 140.9 (s), 153.9 (s); HRMS *m*/*e* (M^+) calcd 486.169, obsd 486.169.

(*R*)-(+)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-9,12-dithia-10,11-(1,2-benzo)cyclotetradeca-2,4-diene (32). According to the procedure described for the synthesis of **22**, from (*R*)-**21** and 1,2-dimercaptobenzene: yield 72%; mp 222.2−223.9 °C; $[\alpha]_D$ = +345.6 (*c* = 0.544, THF), $[\alpha]_{578}$ = +381.6, $[\alpha]_{546}$ = +448.9, $[\alpha]_{436}$ = +981.8, $[\alpha]_{365}$ = +2873; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.94−3.09 (m, 2 H), 3.18−3.30 (m, 2 H), 4.13−4.33 (m, 4 H), 7.06−7.47 (m, 12 H), 7.86 (d, J = 8.0 Hz, 2 H), 7.92 (d, J = 9.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 34.8 (t), 67.6 (t), 100.1 (s), 115.5 (d), 120.1 (s), 123.6 (d), 125.4 (d), 126.3 (d), 127.7 (d), 127.8 (d), 129.3 (s), 129.3 (s), 133.4 (d), 134.1 (s), 138.6 (s), 154.0 (s); HRMS *m*/*e* (M^+) calcd 480.122, obsd 480.122.

(*S*)-(−)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-10,15-dithia-12,13-(1,2-benzo)cyclooctadeca-2,4-diene (33). According to the procedure described for the synthesis of **22**, from (*S*)-**20** and 1,2-bis(mercaptomethyl)benzene: yield 61%; mp 75.9−77.8 °C; $[\alpha]_D$ = −160.8 (*c* = 0.306, THF), $[\alpha]_{578}$ = −177.8, $[\alpha]_{546}$ = −210.8, $[\alpha]_{436}$ = −491.5, $[\alpha]_{365}$ = −1587; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.85−2.02 (m, 4 H), 2.44−2.67 (m, 4 H), 3.98 (AB-system, J_1 = 62.0 Hz, J_2 = 12.0 Hz, 4 H), 3.97−4.08 (m, 2 H), 4.35−4.47 (m, 2 H), 7.34−7.51 (m, 10 H), 7.54 (d, J = 9.0 Hz, 2 H), 8.03 (d, J = 8.1 Hz, 2 H), 8.09 (d, J = 9.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 29.3 (t), 29.6 (t), 34.4 (t), 67.6 (t), 115.2 (d), 120.4 (s), 123.7 (d), 125.5 (d), 126.5 (d), 127.8 (d), 128.1 (d), 129.4 (s), 129.5 (d), 130.6 (d), 134.4 (s), 136.4 (s), 154.1 (s); HRMS *m*/*e* (M^+) calcd 536.184, obsd 536.184.

(*R*)-(−)-2,2′-Dimethoxy-1,1′-binaphthyl-3,3′-dicarbaldehyde (37). A solution of (*R*)-**36** (12.56 g, 40.0 mmol) and TMEDA (31.4 mL, 209 mmol) in Et_2O (600 mL) was cooled to 0 °C. A 2.0 M solution of *n*-BuLi in hexanes (87 mL, 174 mmol) was added dropwise over a period of 30 min. The mixture was stirred at 0 °C for 1 h and was then slowly warmed to reflux. After being refluxed for 16 h the resulting pale brown suspension was cooled to 0 °C and DMF (25 mL, 320 mmol) was added dropwise. The mixture was stirred at 0 °C for 90 min, and then 4 N HCl (120 mL, 480 mmol) was added slowly under vigorous stirring. The resulting two-phase system was stirred for 30 min. The organic layer was separated, washed with 0.5 N HCl (200 mL), a saturated $NaHCO_3$ solution (200 mL), and brine (200 mL), dried (Na_2SO_4), and concentrated under reduced pressure to give a yellow solid (14.36 g). The crude product was filtered over a short column (silica gel, Et_2O) and then recrystallized from 96% EtOH to give **37** (76%) as pale yellow crystals: mp 156.5−158.3 °C (lit.[65] racemate, mp 150 °C); $[\alpha]_D$ = −29.1 (*c* = 0.850, CH_2Cl_2), $[\alpha]_{578}$ = −31.8, $[\alpha]_{546}$ = −37.9, $[\alpha]_{436}$ = −83.2; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.52 (s, 6 H), 7.17−7.55 (m, 6 H), 8.08 (d, J = 7.3 Hz, 2 H), 8.64 (s, 2 H), 10.58 (s, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 63.1 (q), 124.9 (s), 125.5 (d), 126.1 (d), 128.5 (s), 129.6 (d), 129.9 (s), 130.5 (d), 132.3 (d), 137.0 (s), 156.5 (s), 190.3 (d).

(*S*)-(+)-37. By the same procedure (*S*)-**37** (75%) was obtained: mp 156.3−157.7 °C; $[\alpha]_D$ = +28.6 (*c* = 1.210, CH_2Cl_2), $[\alpha]_{578}$ = +30.9, $[\alpha]_{546}$ = +38.1, $[\alpha]_{436}$ = +79.9.

Determination of the Extent of Racemization in the Synthesis of 37. (*R*)-**37** (5 mg) and (*S*)-**37** (9 mg) were dissolved in *n*-hexane/2-propanol 9:1 (2 mL). A sample of this mixture was analyzed by HPLC on a OT-column (eluent *n*-hexane/2-propanol 9:1, flow 0.5 mL/min). The retention times of the enantiomers were (*R*) 34.39 min, (*S*) 36.83 min.

From analogous HPLC-analysis of (*S*)-**37**, purified by column chromatography, but not crystallized, it was observed that this material was enantiomerically pure.

(*R*)-(−)-3,3′-Bis(hydroxymethyl)-2,2′-dimethoxy-1,1′-binaphthyl (38).[27] (*R*)-**38** was prepared by a modified procedure as described for the synthesis of (*S*)-**38**.[27] To a solution of (*R*)-**37** (6.15 g, 16.6 mmol) in a mixture of absolute ethanol (130 mL) and THF (20 mL) was added $NaBH_4$ (1.25 g, 33.0 mmol) at room temperature. After being stirred for 4 h the reaction mixture was concentrated under reduced pressure. The residue was taken up in CH_2Cl_2 (200 mL) and 3 N HCl (200 mL) and was vigorously stirred untill all solid material was dissolved. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 150 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to give **38** (95%) as a white foam: mp 182.6−184.2 °C; $[\alpha]_D$ = −46.8 (*c* = 0.602, THF), $[\alpha]_{578}$ = −53.8, $[\alpha]_{546}$ = −63.1, $[\alpha]_{436}$ = −123.6, $[\alpha]_{365}$ = −188.2; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.79 (s, br, 2 H), 3.30 (s, 6 H), 4.97 (AB-system, J_1 = 28.2 Hz, J_2 = 13.2 Hz, 4 H), 7.15−7.44 (m, 6 H), 7.89 (d, J = 88.3 Hz, 2 H), 8.03 (s, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 60.8 (q), 62.0 (t), 124.0 (s), 125.0 (d), 125.6 (d), 126.5 (d), 128.1 (d), 128.3 (d), 130.6 (s), 133.9 (s), 134.0 (s), 154.7 (s).

(*S*)-(+)-38.[27] By the same procedure (*S*)-**38** (91%) was obtained: mp 181.8−183.9 °C (lit.[27] mp 183−185 °C); $[\alpha]_D$ =

(65) Moneta, W.; Baret, P.; Pierre, J.-L. *Bull. Soc. Chim. Fr.* **1988**, 995.

+47.4 (c = 0.814, THF) (lit.[27] $[\alpha]_D$ = +53.4), $[\alpha]_{578}$ = +55.0, $[\alpha]_{546}$ = +65.6, $[\alpha]_{436}$ = +127.4, $[\alpha]_{365}$ = +195.3.

1,4,8-Trithiaoctane. This product was obtained as a side product (8%) in the synthesis of 1,4,8,11-tetrathiaundecane[8b] bp 120−135 °C (0.35 mm Hg); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.36 (t, J = 8.1 Hz, 1 H), 1.66−1.84 (m, 3 H), 2.52−2.71 (m, 8 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 23.4 (t), 24.7 (t), 30.2 (t), 33.3 (t), 36.0 (t).

(*S*)-(+)-2,3,4:5,6,7-Bis[1,3-(2-methoxynaphtho)]-9,12,15-trithiacyclopentadeca-3,5-diene (40). According to the procedure described for the synthesis of **22**, from (*S*)-**39** and 1,4,7-trithiaheptane: yield 76% as a white solid; mp 272.2−274.1 °C; $[\alpha]_{578}$ = +969 (c = 0.342, THF), $[\alpha]_{546}$ = +1133, $[\alpha]_{436}$ = +2306, $[\alpha]_{365}$ = +4865; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.57−2.68 (m, 2 H), 2.88−3.15 (m, 6 H), 3.07 (s, 6 H), 3.97 (AB-system, J_1 = 103.8 Hz, J_2 = 13.7 Hz, 4 H), 7.22−7.47 (m, 6 H), 7.90 (d, J = 8.1 Hz, 2 H), 7.96 (s, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 30.8 (t), 32.1 (t), 32.3 (t), 61.0 (q), 124.1 (s), 124.9 (d), 125.5 (d), 126.4 (d), 128.1 (d), 130.0 (d), 131.2 (s), 133.3 (s), 134.5 (s), 155.1 (s); HRMS m/e (M^+) calcd 492.125, obsd 492.125.

(*R*)-(−)-2,3,4:5,6,7-Bis[1,3-(2-methoxynaphtho)]-9,12,16-trithiacyclohexadeca-3,5-diene (41). According to the procedure described for the synthesis of **22**, from (*R*)-**39** and 1,4,8-trithiaoctane: yield 50% as a white solid; mp 215.6−217.3 °C; $[\alpha]_D$ = −797.5 (c = 0.276, THF), $[\alpha]_{578}$ = −870.7, $[\alpha]_{546}$ = −1019, $[\alpha]_{436}$ = −2089, $[\alpha]_{365}$ = −4479; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.77−1.92 (m, 2 H), 2.11−2.97 (m, 8 H), 3.10 (s, 3 H), 3.14 (s, 3 H), 3.96 (AB-system, J_1 = 106.0 Hz, J_2 = 13.7 Hz, 2 H), 4.01 (AB-system, J_1 = 125.8 Hz, J_2 = 13.3 Hz, 2 H), 7.21−7.31 (m, 4 H), 7.37−7.46 (m, 2 H), 7.87−7.92 (m, 2 H), 8.02 (s, 1 H), 8.10 (s, 1 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 28.2 (t), 29.1 (t), 30.0 (t), 31.4 (t), 31.6 (t), 31.8 (t), 33.9 (t), 60.9 (q), 124.0 (s), 124.1 (s), 124.9 (d), 125.6 (d), 126.4 (d), 128.0 (d), 130.6 (d), 130.8 (d), 131.1 (s), 131.1 (s), 132.9 (s), 133.3 (s), 133.4 (s), 134.5 (s), 155.0 (s), 155.7 (s); HRMS m/e (M^+) calcd 506.141, obsd 506.141.

(*R*)-(−)-2,3,4:5,6,7-Bis[1,3-(2-methoxynaphtho)]-9,12,-15,18-tetrathiacyclooctadeca-3,5-diene (42). According to the procedure described for the synthesis of **22**, from (*R*)-**39** and 1,4,7,10-tetrathiadecane: yield 44% as a white solid; mp 182.2−183.5 °C; $[\alpha]_D$ = −590.6 (c = 0.384, THF), $[\alpha]_{578}$ = −642.7, $[\alpha]_{546}$ = −750.5, $[\alpha]_{436}$ = −1508, $[\alpha]_{365}$ = −3077; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.58−2.77 (m, 12 H), 3.29 (s, 6 H), 4.04 (AB-system, J_1 = 91.2 Hz, J_2 = 14.2 Hz, 4 H), 7.11−7.28 (m, 4 H), 7.37−7.45 (m, 2 H), 7.91 (d, J = 8.2 Hz, 2 H), 8.14 (s, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 29.6 (t), 31.5 (t), 32.00 (t), 32.3 (t), 61.2 (q), 124.4 (s), 125.0 (d), 125.7 (d), 126.4 (d), 127.9 (d), 130.7 (d), 130.9 (s), 133.3 (s), 133.5 (s), 154.8 (s); HRMS m/e (M^+) calcd 552.129, obsd 552.128.

(*R*)-(−)-2,3,4:5,6,7-Bis[1,3-(2-methoxynaphtho)]-9,12,-16,19-tetrathiacyclononadeca-3,5-diene (43). According to the procedure described for the synthesis of **22**, from (*R*)-**39** and 1,4,8,11-tetrathiaundecane: yield 40% as a white solid; mp 132.4−133.6 °C; $[\alpha]_D$ = −178.7 (c = 0.282, THF), $[\alpha]_{578}$ = −195.4, $[\alpha]_{546}$ = −228.7, $[\alpha]_{436}$ = −462.1, $[\alpha]_{365}$ = −886.2; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.62 (quintet, J = 7.5 Hz, 2 H), 1.96−2.10 (m, 2 H), 2.22−2.36 (m, 2 H), 2.51−2.77 (m, 8 H), 3.39 (s, 6 H), 4.04 (AB-system, J_1 = 71.2 Hz, J_2 = 14.1 Hz, 4 H), 7.06−7.45 (m, 6 H), 7.90 (d, J = 7.7 Hz, 2 H), 8.13 (s, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 29.5 (t), 30.1 (t), 30.3 (t), 30.6 (t), 31.8 (t), 61.2 (q), 124.6 (s), 125.0 (d), 125.6 (d), 126.4 (d), 127.8 (d), 130.6 (d), 130.8 (s), 132.4 (s), 133.6 (s), 155.0 (s); HRMS m/e (M^+) calcd 566.144, obsd 566.144.

(*S*)-(+)-2,3,4:5,6,7-Bis[1,3-(2-methoxynaphtho)]-9,13,18,-22-tetrathiacyclodoeicosa-3,5-diene (44). According to the procedure described for the synthesis of **22**, from (*S*)-**39** and 1,5,10,14-tetrathiatetradecane: yield 56% as a colorless oil; $[\alpha]_D$ = +5.7 (c = 0.246, THF), $[\alpha]_{578}$ = +6.1, $[\alpha]_{546}$ = +8.9, $[\alpha]_{436}$ = +31.7, $[\alpha]_{365}$ = +69.1; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.34−1.57 (m, 4 H), 1.73−1.97 (m, 4 H), 2.20−2.30 (m, 4 H), 2.52 (t, J = 7.4 Hz, 4 H), 2.65 (t, J = 7.2 Hz, 4 H), 3.39 (s, 6 H), 4.03 (AB-system, J_1 = 35.4 Hz, J_2 = 13.2 Hz, 4 H), 7.14−7.27 (m, 4 H), 7.36−7.44 (m, 2 H), 7.88 (d, J = 8.1 Hz, 2 H), 8.04 (s, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 28.8 (t), 29.9 (t), 30.8 (t), 30.9 (t), 31.2 (t), 31.5 (t), 61.2 (q), 124.6 (s), 124.9 (d), 125.7 (d), 126.2 (d), 127.8 (d), 130.2 (d), 130.6 (s), 132.1 (s), 133.6 (s), 155.1 (s); HRMS m/e (M^+) calcd 608.191, obsd 608.191.

(*S*)-(−)-3,3′-Bis(bromomethyl)-2,2′-dihydroxy-1,1′-binaphthyl (45). To a cooled (0 °C) solution of (*S*)-**39** (0.75 g, 1.50 mmol) in CH_2Cl_2 (50 mL) was added dropwise BBr_3 (1.0 M in CH_2Cl_2, 4.0 mL, 4.0 mmol). After the mixture was stirred at room temperature for 4 h a saturated $NaHCO_3$ solution (10 mL) was added. The mixture was poured into water (100 mL) and was extracted with CH_2Cl_2 (3 × 75 mL). The combined organic layers were washed with 2 N HCl (100 mL), dried ($MgSO_4$), and concentrated under reduced pressure to give **45** (99%) as a pale yellow foam: mp 186.4−188.6 °C; $[\alpha]_D$ = −165.9 (c = 0.340, THF), $[\alpha]_{578}$ = −175.3, $[\alpha]_{546}$ = −207.6, $[\alpha]_{436}$ = −474.4; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.82 (AB-system, J_1 = 11.3 Hz, J_2 = 10.2 Hz, 4 H), 5.34 (s, 2 H), 7.08−7.13 (m, 2 H), 7.27−7.45 (m, 4 H), 7.88−7.93 (m, 2 H), 8.09 (s, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 28.9 (t), 111.4 (s), 124.1 (d), 124.7 (d), 126.6 (s), 128.2 (d), 128.5 (d), 129.1 (s), 132.3 (d), 133.4 (s), 150.8 (s); HRMS m/e (M^+) calcd 469.952, obsd 469.951.

(*S*)-(−)-2,2′-Bis(methyoxymethoxy)-1,1′-dinaphthyl (47). (*S*)-**47** was prepared by a modified procedure as described for the synthesis of racemic **47**.[66] To a solution of (*S*)-**10** (2.75 g, 9.62 mmol) in THF (100 mL) was added KO^{t}Bu (2.37 g, 21.1 mmol). After the mixture was stirred at room temperature for 10 min a solution of freshly prepared methoxymethyl iodide[67] (3.64 g, 21.2 mmol) in THF (15 mL) was added dropwise over a period of 15 min. The mixture was stirred for 18 h at room temperature and was then concentrated under reduced pressure. Water (100 mL) was added to the residue, and the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with 2 N NaOH (100 mL), dried ($MgSO_4$), and concentrated under reduced pressure to give a viscous yellow oil (3.53 g). The crude product was purified by column chromatography (silica gel, CH_2Cl_2) to give **47** (96%) as a pale yellow oil that crystallized on standing: mp 95.1−96.6 °C (lit.[66] racemate: mp 93−94 °C); $[\alpha]_D$ = −79.0 (c = 0.990, THF), $[\alpha]_{578}$ = −83.4, $[\alpha]_{546}$ = −98.4, $[\alpha]_{436}$ = −223.8, $[\alpha]_{365}$ = −690.9; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.20 (s, 6 H), 5.08 (AB-system, J_1 = 22.2 Hz, J_2 = 6.2 Hz, 4 H), 7.13−7.44 (m, 6 H), 7.64 (d, J = 9.2 Hz, 2 H), 7.93 (d, J = 8.1 Hz, 2 H), 8.00 (d, J = 9.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 55.8 (q), 95.2 (t), 117.3 (d), 121.3 (s), 124.1 (d), 125.6 (d), 126.3 (d), 127.9 (d), 129.4 (d), 129.9 (s), 134.1 (s), 152.7 (s); HRMS m/e (M^+) calcd 374.152, obsd 374.152.

(*S*)-(−)-2,2′-Bis(methyoxymethoxy)-1,1′-dinaphthyl-3,3′-dicarbaldehyde (48). To a cooled (0 °C) solution of (*S*)-**47** (2.96 g, 7.91 mmol) and TMEDA (6.0 mL, 39 mmol) in Et_2O (350 mL) was added dropwise *n*-BuLi (1.6 M in hexanes, 21.2 mL, 33.9 mmol) over a period of 15 min. After being stirred at 0 °C for 2 h, the mixture was refluxed for 17 h. The resulting purple-brown suspension was cooled to 0 °C, and DMF (5.0 mL, 65 mmol) was added. The mixture was stirred for 2 h at 0 °C, and then a saturated NH_4Cl solution (50 mL) was added dropwise. The organic layer was separated, washed with water (150 mL), a saturated $NaHCO_3$ solution (150 mL) and brine (150 mL), dried ($MgSO_4$), and concentrated under reduced pressure to give an orange oil (2.92 g). The crude product was purified by column chromatography (silica gel, CH_2Cl_2) to give **48** (78%) as a pale yellow solid: mp 126.7−128.6 °C; $[\alpha]_D$ = −43.9 (c = 0.440, THF), $[\alpha]_{578}$ = −47.4, $[\alpha]_{546}$ = −60.2; ^{1}H NMR (DMSO-d_6, 200 MHz) δ 2.67 (s, 6 H), 4.75 (AB-system, J_1 = 9.4 Hz, J_2 = 6.0 Hz, 4 H), 7.10 (d, J = 8.1 Hz, 2 H), 7.43−7.60 (m, 4 H), 8.27 (d, J = 8.1 Hz, 2 H), 8.70 (s, 2 H), 10.40 (s, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 57.0 (q), 100.6 (t), 125.9 (s), 126.1 (d), 126.3 (d), 128.9 (s), 129.6 (d), 130.0 (s), 130.3 (d), 132.3 (d), 136.7 (s), 154.0 (s), 190.6 (d); HRMS m/e (M^+) calcd 430.142, obsd 430.142.

(*S*)-(+)-3,3′-Bis(hydroxymethyl)-2,2′-bis(methyoxymethoxy)-1,1′-dinaphthyl (49). (*S*)-**49** was prepared by a different approach as described for the synthesis of racemic **49**.[21b] To a solution of (*S*)-**48** (1.33 g, 3.09 mmol) in absolute ethanol (100 mL) and THF (20 mL) was added $NaBH_4$ (0.24

(66) Peacock, S. S.; Walba, D. M.; Gaeta, F. C. A.; Helgeson, R. C.; Cram, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 2043.
(67) Jung, M. E.; Mazurek, M. A.; Lim, R. M. *Synthesis* **1978**, 588.

g, 6.3 mmol). After being stirred at room temperature for 17 h the mixture was concentrated under reduced pressure to give a yellow foam (2.02 g). The crude product was boiled in CH_2Cl_2 (3 × 50 mL) and decanted while hot. The combined organic layers were concentrated under reduced pressure to give **49** (95%) as a pale yellow foam (lit.[21b] racemate is a colorless oil): mp 68.6−69.2 °C; $[\alpha]_D$ = +66.4 (*c* = 0.256, THF), $[\alpha]_{578}$ = +69.9, $[\alpha]_{546}$ = +80.9, $[\alpha]_{436}$ = +151.6; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.20 (s, 6 H), 3.54 (s, br, 2 H), 4.47 (AB-system, J_1 = 8.3 Hz, J_2 = 6.2 Hz, 4 H), 4.93 (AB-system, br, J_1 = 30.5 Hz, J_2 = 12.7 Hz, 4 H), 7.14−7.48 (m, 6 H), 7.92 (d, *J* = 8.1 Hz, 2 H), 8.04 (s, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 57.1 (q), 61.8 (t), 99.3 (t), 125.2 (s), 125.4 (d), 125.8 (d), 126.8 (d), 128.2 (d), 129.7 (d), 130.9 (s), 133.8 (s), 134.6 (s), 153.1 (s); HRMS *m*/*e* (M^+) calcd 434.173, obsd 434.173.

2,3-[1,2-naphtho]4,5-[1,2-(3-formylnaphtho)]-1,6-dioxacyclohepta-2,4-diene (52) and 2,3:4,5-Bis[1,2-(3-formylnaphtho)]-1,6-dioxacyclohepta-2,4-diene (53). To a cooled (0 °C) solution of **51** (2.00 g, 6.71 mmol) and TMEDA (5.2 mL, 35 mmol) in Et_2O (150 mL) was added dropwise *s*-BuLi (0.8 M in cyclohexane/isopentane, 34 mL, 27 mmol) over a period of 15 min. The resulting dark green solution was allowed to warm to room temperature. After being stirred at ambient temperature for 17 h the mixture was cooled to 0 °C and DMF (4.2 mL, 53 mmol) was added. After the mixture was stirred at 0 °C for 2 h, 4 N HCl (20 mL, 80 mmol) was added dropwise. The organic layer was washed with water (150 mL), a saturated $NaHCO_3$ solution (150 mL), and brine (150 mL), dried ($MgSO_4$), and concentrated under reduced pressure to give a pale yellow solid (1.82 g). The crude product was purified by column chromatography over a 30 cm silica gel column (100 g silica gel, CH_2Cl_2) to give **52** (18%) as a first fraction (R_f = 0.52) and **53** (29%) as a second fraction (R_f = 0.22). Analytically pure **53** was obtained by recrystallization from $CHCl_3$/*n*-hexane.

52: mp 182.1−184.0 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.81 (AB-system, J_1 = 4.7 Hz, J_2 = 3.4 Hz, 2 H), 7.40−7.58 (m, 7 H), 7.95−8.10 (m, 3 H), 8.60 (s, 1 H), 10.62 (s, 1 H); ^{13}C NMR (DMSO-d_6, 50.3 MHz) δ 103.4 (t), 121.1 (d), 124.5 (s), 125.2 (d), 125.6 (d), 125.9 (d), 126.1 (d), 126.6 (d), 126.8 (s), 127.5 (s), 128.7 (d), 129.1 (d), 130.2 (s), 130.8 (d), 131.0 (d), 131.1 (d), 131.3 (s), 131.4 (s), 134.0 (s), 150.8 (s), 151.2 (s), 189.9 (d); HRMS *m*/*e* (M^+) calcd 326.094, obsd 326.094.

53: mp 238.9−240.7 °C; ^{1}H NMR (DMSO-d_6, 200 MHz) δ 6.04 (s, 2 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 7.47−7.64 (m, 4 H), 8.32 (d, *J* = 8.1 Hz, 2 H), 8.71 (s, 2 H), 10.51 (s, 2 H); ^{13}C NMR (DMSO-d_6, 50.3 MHz) δ 104.3 (t), 125.8 (d), 126.0 (s), 126.3 (d), 127.3 (s), 129.3 (d), 130.3 (s), 130.8 (d), 131.5 (d), 133.9 (s), 150.9 (s), 189.8 (d); HRMS *m*/*e* (M^+) calcd 354.089, obsd 354.089. Anal. Calcd (found) for $C_{23}H_{14}O_4 \cdot CHCl_3$: C, 60.73 (60.70); H, 3.19 (3.24); Cl, 22.41 (21.03).

7,7,9,9-Tetramethyl-2,3:4,5-di(1,2-naphtho)-1,6,8-trioxa-7,9-disilacyclonona-2,4-diene (56). To a solution of **10** (2.38 g, 8.32 mmol) in CH_2Cl_2 (50 mL) were added Et_3N (3.5 mL, 25 mmol) and dichlorodimethylsilane (0.93 mL, 7.7 mmol). After being refluxed for 18 h the reaction mixture was washed with water (2 × 50 mL), a saturated NH_4Cl solution (50 mL), and 2 N NaOH (2 × 50 mL), dried ($MgSO_4$), and concentrated under reduced pressure to give a brown solid (0.70 g). The crude product was purified by column chromatography (silica gel, CH_2Cl_2) to give **56** (17%) as a pale yellow powder: mp 172.2−174.6 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ −0.55 (s, 6 H), 0.27 (s, 6 H), 7.19−7.43 (m, 8 H), 7.89−7.97 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ −1.3 (q), 0.2 (q), 121.9 (d), 123.4 (s), 124.2 (d), 125.2 (d), 126.6 (d), 127.8 (d), 129.6 (d), 130.0 (s), 134.2 (s), 150.4 (s); HRMS *m*/*e* (M^+) calcd 416.126, obsd 416.126.

(*R*)-(+)-2,2′-Bis(2-propen-1-yloxy)-1,1′-dinaphthyl (59). A solution of (*R*)-**10** (1.43 g, 5.00 mmol), allyl bromide (2.42 g, 20.0 mmol), and K_2CO_3 (2.76 g, 20.0 mmol) in acetone (150 mL) was refluxed for 70 h. The reaction mixture was filtered and concentrated under reduced pressure to give pale yellow crystals (1.82 g). The crude product was purified by column chromatography (silica gel, CH_2Cl_2) to give **59** (99%) as white crystals: mp 110.1−111.1 °C; $[\alpha]_D$ = +29.3 (*c* = 0.382, THF), $[\alpha]_{578}$ = +32.5, $[\alpha]_{546}$ = +41.1, $[\alpha]_{436}$ = +138.5, $[\alpha]_{365}$ = +667.8; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.60−4.62 (m, 4 H), 5.06−5.16 (m, 4 H), 5.75−5.94 (m, 2 H), 7.27−7.45 (m, 8 H), 7.49 (d, *J* = 9.0 Hz, 2 H), 7.96 (d, *J* = 8.0 Hz, 2 H), 8.02 (d, *J* = 9.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 70.0 (t), 115.7 (d), 116.5 (t), 120.4 (s), 123.7 (d), 125.6 (d), 126.3 (d), 128.0 (d), 129.2 (d), 129.4 (s), 133.8 (d), 134.2 (s), 154.1 (s); HRMS *m*/*e* (M^+) calcd 366.162, obsd 366.162.

1,13-Bis[3-(2-methoxynaphthyl)]-2,5,9,12-tetrathiatridecane (62). To a solution of 1,4,8,11-tetrathiaundecane (1.14 g, 5.00 mmol) in THF (50 mL) was added KO^{t}Bu (1.40 g, 12.5 mmol). After the mixture was stirred at room temperature for 20 min **61** (2.51 g, 10.0 mmol) was added. The mixture was stirred at ambient temperature for 4 h. The resulting pale brown suspension was concentrated under reduced pressure. 2 N HCl (100 mL) was added to the residue, and the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to give a yellow oil (2.92 g). The crude product was purified by column chromatography (silica gel, CH_2Cl_2) to give **62** (100%) as a colorless oil that solidifies on standing: mp 78.6−80.4 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.75 (quintet, *J* = 7.2 Hz, 2 H), 2.54 (t, *J* = 7.2 Hz, 4 H), 2.69−2.73 (m, 8 H), 3.93 (s, 4 H), 3.97 (s, 6 H), 7.14 (s, 2 H), 7.32−7.48 (m, 4 H), 7.69 (s, 2 H), 7.72−7.77 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 29.3 (t), 30.8 (t), 31.1 (t), 31.7 (t), 32.0 (t), 55.5 (q), 105.5 (d), 123.9 (d), 126.2 (d), 126.4 (d), 127.3 (d), 128.3 (s), 128.5 (s), 129.0 (d), 134.0 (s), 155.8 (s); HRMS *m*/*e* (M^+) calcd 568.160, obsd 568.160.

1,13-Bis[3-(2-hydroxynaphthyl)]-2,5,9,12-tetrathiatridecane (63). To a cooled (0 °C) solution of **62** (1.58 g, 2.78 mmol) in CH_2Cl_2 (50 mL) was added BBr_3 (1.6 mL, 16.7 mmol) dropwise over a period of 5 min. After the mixture was stirred at room temperature for 20 h a saturated $NaHCO_3$ solution (20 mL) was added. The mixture was stirred for 30 min and was then poured into water (100 mL). The mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with 3 N HCl (100 mL), dried ($MgSO_4$), and concentrated under reduced pressure to give a yellow oil (1.71 g) that solidified on standing. The crude product was boiled in toluene (50 mL) and decanted while hot. The decantate was cooled to −20 °C to give **63** (83%) as a white powder: mp 97.2−99.3 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.58 (quintet, *J* = 7.1 Hz, 2 H), 2.36 (t, *J* = 7.1 Hz, 4 H), 2.64 (s, 8 H), 3.99 (s, 4 H), 6.48 (s, br, 2 H), 7.26 (s, 2 H), 7.27−7.45 (m, 4 H), 7.61−7.74 (m, 6 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 29.0 (t), 30.6 (t), 30.9 (t), 31.8 (t), 32.6 (t), 111.7 (d), 124.0 (d), 125.3 (s), 126.3 (d), 126.5 (d), 127.4 (d), 128.7 (s), 129.6 (d), 134.3 (s), 152.8 (s); HRMS *m*/*e* (M^+) calcd 540.129, obsd 540.129.

Acknowledgment. We thank the Dutch Organization of Scientific Research (NWO) administered through the Office for Chemical Research (SON) for financial support of this work.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of thiocrown ethers **22**−**33** and **40**−**44**; descriptions of attempts to demethylate **40**, **42**, and **43**; attempts to brominate **49** and to cyclize **45**; attempted synthesis of **58**; attempts to prepare **64** by oxidative coupling (75 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO952107O